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PHOTOCHEMICAL AND THERMAL TRANSFORMATIONS
OF A FEW HETEROHEXATRIENES,
DIBENZOBARRELENES AND RELATED SYSTEMS

A Thesis Submitted
in Partial Fulfilment of the Requirements
for the Degree of
DOCTOR OF PHILOSOPHY

By
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to the
DEPARTMENT OF CHEMISTRY
INDIAN INSTITUTE OF TECHNOLOGY, KANPUR
JUNE, 1981

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TO
MY MOTHER
AND
TO THE MEMORY OF
MY FATHER

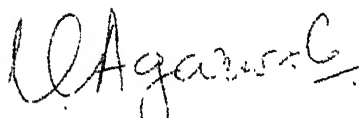
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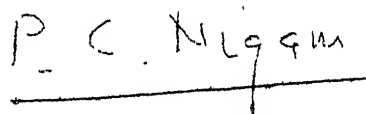
This is to certify that Mr. Challa Vijaya Kumar has satisfactorily completed all the courses required for the Ph.D. degree programme. These courses include:

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Mr. Challa Vijaya Kumar successfully completed his Ph.D. Qualifying Examination in January 1977.



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CERTIFICATE II

Certified that the work embodied in this thesis entitled: "PHOTOCHEMICAL AND THERMAL TRANSFORMATIONS OF A FEW HETEROHEXATRIENES, DIBENZOBARRELENEs AND RELATED SYSTEMS" has been carried out by Mr. Challa Vijaya Kumar under my supervision and the same has not been submitted elsewhere for a degree.


M. V. GEORGE
Thesis Supervisor


21.8.1981

BL

STATEMENT

I hereby declare that the matter embodied in this thesis is the result of investigations carried out by me in the Department of Chemistry, Indian Institute of Technology, Kanpur, India, under the supervision of Professor M. V. George.

In keeping with the general practice of reporting scientific observations, due acknowledgement has been made wherever the work described is based on the findings of other investigators.


Challa Vijaya Kumar

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CONTENTS

	Page
CERTIFICATE I	ii
CERTIFICATE II	iii
STATEMENT	iv
ACKNOWLEDGEMENTS	v
PREFACE	ix
CHAPTER I Photochemical and Thermal Transformations of a Few <u>cis</u> -1,2-Dibenzoylalkenes	1
CHAPTER II Photochemical and Thermal Transformations of Some Dibenzobarrelene Derivatives	60
CHAPTER III Photochemical and Thermal Transformations of 2H-1,2,4- Benzothiadiazine 1,1-Dioxides	150
VITAE	xvi

PREFACE

The thesis entitled: "Photochemical and Thermal Transformations of a Few Heterohexatrienes, Dibenzobarrelenes and Related Systems" is divided into three chapters. Chapter 1 deals with a brief survey of the photochemical transformations of heterohexa-1,3,5-trienes, followed by our studies, employing cis-1,2-dibenzoylalkenes such as, 2,3-dibenzoylbicyclo[2.2.1]-hept-2-ene (1) and 2,3-dibenzoylbicyclo[2.2.2]oct-2-ene (2). Substrates such as (1) and (2) have been chosen for our photochemical studies since the cis-trans-isomerizations of the alkene double bonds in these systems will be prevented by structural constraints.

Irradiation of 1 in dry methanol, for example, gave a 41% yield of methyl 3-(phenoxyphenylmethylene)bicyclo[2.2.1]-heptane-2-exo-carboxylate (3). In contrast, the irradiation of 1 in benzene gave a 15% yield of 3-(phenoxyphenylmethylene)-bicyclo[2.2.1]heptane-2-exo-carboxylic acid (4), as the only isolable product. Similarly, the irradiation of 2 in methanol gave a 20% yield of methyl 3-(phenoxyphenylmethylene)bicyclo[2.2.2]octane-2-carboxylate (5). On the other hand, the irradiation of 2 in methanol using a Hanovia 450-W medium-pressure

lamp source, with pyrex filter gave a 5% yield of the lactone 6, as the only isolable product. Interestingly, the irradiation of 2 in benzene solution in a Srinivasan-Griffin Rayonet photochemical reactor with 3500 Å light source, resulted in the formation of a mixture of products consisting of the lactone 6 (20%) and 3-(phenoxyphenylmethylene)bicyclo[2.2.2]-octane-2-carboxylic acid (7, 7%). It has been shown that the base-catalysed hydrolysis of the ester 5 leads to the acid 7, in agreement with the assigned structures for these compounds.

Laser flash-photolysis studies of 1 and 2 reveal that diradical intermediates may be involved in their transformation to different products.

In continuation of our studies we have examined the thermal transformations of 1 and 2. Heating of 1 around 370° for 1 hr resulted in the formation of a 26% yield of 2-endo-3-exo-dibenzoylbicyclo[2.2.1]heptane (8), presumably arising through a disproportionation reaction. In contrast, the thermolysis of 2 (310°) resulted in the formation of a 42% yield of 2-benzoyl-3-phenylbicyclo[2.2.2]oct-2-ene (9), which may arise through the decarbonylation of the lactonic intermediate 6.

Reasonable mechanisms have been suggested for the formation of the different products in the thermal and photochemical transformations of 1 and 2.

Chapter 2 of the thesis deals with our studies on the photochemical and thermal transformations of a few barrelene derivatives containing the cis-1,2-dibenzoylalkene moiety. These include 11,12-dibenzoyl-9,10-dihydro-9,10-ethenoanthracene (10), 11,12-dibenzoyl-9,10-dihydro-9-methyl-9,10-ethenoanthracene (11), 11,12-dibenzoyl-9,10-dihydro-9-hydroxy-9,10-ethenoanthracene (12) and 11,12-dibenzoyl-9,10-dihydro-9,10-dimethyl-9,10-ethenoanthracene (13).

Irradiation of 10 in methanol, for example, gave a 52% yield of 1,2-dibenzoyldibenzotricyclo[3.3.0.0^{2,8}]-octa-3,6-diene (14) and a small amount (4%) of benzoic acid. It was observed that the yield of benzoic acid increased (22%) when the irradiation of 10 was carried out in methanol, saturated with oxygen. Irradiation of 10 in acetone however, gave a 89% yield of 14. Catalytic hydrogenation of 14 over palladium on calcium carbonate gave 9a,10-dibenzoyl-4b,9,9a,10-tetrahydro-cis-indeno[1,2-a]indene (15), indicating thereby that the cyclopropane ring of 14 is cleaved under these conditions.

Irradiation of 11 in dry benzene gave a 54% yield of 8c,8d-dibenzoyl-4b,8b,8c,8d-tetrahydro-4b-methyldibenzo-[a,b]cyclopropa[c,d]pentalene (16) and a small amount (12%) of benzoic acid. Similar results have been obtained in the irradiation of 11 in solvents such as methanol and acetone. Catalytic hydrogenation of 16 over palladium on calcium carbonate gave 9a,10-dibenzoyl-4b,9,9a,10-tetrahydro-4b-methyl-cis-indeno[1,2-a]indene (17). The fact that 17 is formed from 16 would suggest that the methyl group in 16 is not attached to the cyclopropane ring and that the photorearrangement of 11 leads to the semibullvalene 16.

Irradiation of the hydroxybarrelene derivative 12, in benzene, on the other hand, gave a mixture of products consisting of 9a,10-dibenzoyl-4b,9,9a,10-tetrahydro-9-oxo-cis-indeno[1,2-a]indene (18, 26%) and benzoic acid (4%). Similar results have been obtained when the irradiation of 12 was carried out in acetone.

In contrast to the photoreactions of 10, 11 and 12, the irradiation of 13 gave rise to a mixture of products. Irradiation of 13 in benzene, for example, gave a mixture of 2,3-dibenzoyl-2,3-dihydro-1,4-dimethyl-2-benzonaphthalene

(19, 12%), 1,4-dibenzoyl-5,8-dimethyl-2,6-dibenzocyclooctatetraene (20, 20%), an isomeric hydroxy compound (21, 45%) and benzoic acid (7%). Similarly, irradiation of 13 in methanol gave a mixture of 19 (25%), 20 (27%) and benzoic acid (8%). In contrast, the irradiation of 13 in acetone gave a mixture of 9a,10-dibenzoyl-4b,9,9a,10-tetrahydro-4b-methyl-9-methylene-cis-indeno[1,2-a]indene (22, 80%) and benzoic acid (7%).

In contrast to the photoransformations of the barrelene derivatives such as 10, 11, 12 and 13, their thermal transformations appear to proceed through a retro-Diels-Alder fragmentation mode. Thus, the thermolysis of 11 around 250° (refluxing diphenyl ether) resulted in the isolation of a 23% yield of 9-methylanthracene. Similarly, the thermolysis of 13 under analogous conditions gave a 16% yield of 9,10-dimethylanthracene, along with a small amount of benzoic acid (6%). In contrast, the thermolysis of 12 in refluxing diphenyl ether gave a 26% yield of anthraquinone, besides polymeric materials. Reasonable mechanisms have been suggested for the different products formed in the photochemical and thermal transformations of the barrelene derivatives, 10, 11, 12 and 13.

The results of our studies on the photochemical and thermal transformations of a few 2H-1,2,4-benzothiadiazine 1,1-dioxides which could be the precursors for 1,4,6-thiadiaza-1,3,5-hexatriene systems, forms the subject matter of Chapter 3 of this thesis. The thiadiazine derivatives that we have studied include, 2H-1,2,4-benzothiadiazine-2-phenyl 1,1-dioxide (23), 2H-1,2,4-benzothiadiazine-3-methyl-2-phenyl 1,1-dioxide (24), 2H-1,2,4-benzothiadiazine-3-methyl-2-(2'-methylphenyl) 1,1-dioxide (25), 2H-1,2,4-benzothiadiazine-2-(4'-methylphenyl) 1,1-dioxide (26) and 2H-1,2,4-benzothiadiazine-2-cyclohexyl-3-methyl 1,1-dioxide (27). Irradiation of 23 in methanol, for example, gave a mixture of products consisting of N-(2'-aminobenzenesulfonyl)aniline (28, 72%) and N-(2'-formamidobenzenesulfonyl)aniline (29, 8%). Similarly, the irradiation of 23 in benzene gave a 68% yield of 29. Irradiation of 24 in methanol, on the other hand, gave a 44% yield of 5H-dibenzo[b,g][1,4,6]thiadiazocine-6-methyl 12,12-dioxide (30), whereas in benzene a 25% yield of 30 was obtained. Likewise, the irradiation of 25 in methanol and benzene gave 5H-dibenzo[b,g][1,4,6]thiadiazocine-4,6-dimethyl 12,12-dioxide (31) in 33% and 37% yields, respectively. Similarly, the irradiation of 26 in methanol and benzene gave 5H-dibenzo[b,g][1,4,6]thiadiazocine-2,6-dimethyl 12,12-dioxide (32), in 30% and 46%,

respectively. On the other hand, the irradiation of 27 in benzene, under analogous conditions, did not result in any phototransformation.

In continuation of our studies we have examined the thermal transformations of the thiadiazines 23-27. Heating of 23 in refluxing diphenyl ether for 10 hr, for example, resulted in the formation of a 87% yield of 29. In contrast, the thermolysis of 24, 25 and 26, under analogous conditions did not give rise to any isolable product, except the unchanged starting material, in each case. Heating of 27, in refluxing diphenyl ether, on the other hand, gave a 82% yield of 2-amino-2,3-dihydro-2-methyl-1,3-benzothiazole 1,1-dioxide (33). Reasonable mechanisms have been suggested for the formation of the different products in the photochemical and thermal transformations of the different thiadiazine derivatives (23-27), that we have examined.

CHAPTER I

PHOTOCHEMICAL AND THERMAL TRANSFORMATIONS OF A FEW cis-1,2-DIBENZOYLALKENES

I.1 ABSTRACT

Photochemical and thermal transformations of a few cis-1,2-dibenzoylalkenes such as 2,3-dibenzoylbicyclo[2.2.1]-hept-2-ene (25) and 2,3-dibenzoylbicyclo[2.2.2]oct-2-ene (26) have been studied. Substrates such as 25 and 26 have been chosen for our studies since the cis-trans isomerizations of the alkene double bonds in these systems will be prevented by rigid structural constraints.

Irradiation of 25 in benzene, for example, gave a 15% yield of 3-(phenoxyphenylmethylene)bicyclo[2.2.1]-heptane-2-exo-carboxylic acid (34), as the only isolable product. In contrast, irradiation of 25 in dry methanol gave a 41% yield of methyl 3-(phenoxyphenylmethylene)-bicyclo[2.2.1]heptane-2-exo-carboxylate (33), as the only isolable product. Similarly, the irradiation of 26 in benzene gave a mixture of products consisting of the lactone 38 (20%) and 3-(phenoxyphenylmethylene)bicyclo[2.2.2]octane-2-carboxylic acid (40, 7%). On the other hand, the irradiation of 26 in methanol, in a Srinivasan-Griffin Rayonet photochemical reactor with 3500 Å light source, resulted in a 20% yield of methyl 3-(phenoxyphenylmethylene)bicyclo[2.2.2]octane-2-carboxylate (39). In contrast, the irradiation of 26 in methanol, employing a Hanovia 450-W medium-pressure mercury lamp, provided with a pyrex filter, gave a 5% yield of the lactone 38, as the only isolable product. It has been shown that the base-catalyzed hydrolysis of the ester 39 leads to the acid 40, in agreement with the assigned structures for these compounds.

Laser flash-photolysis studies of 25 and 26 reveal that diradical intermediates may be involved in their transformations to different products.

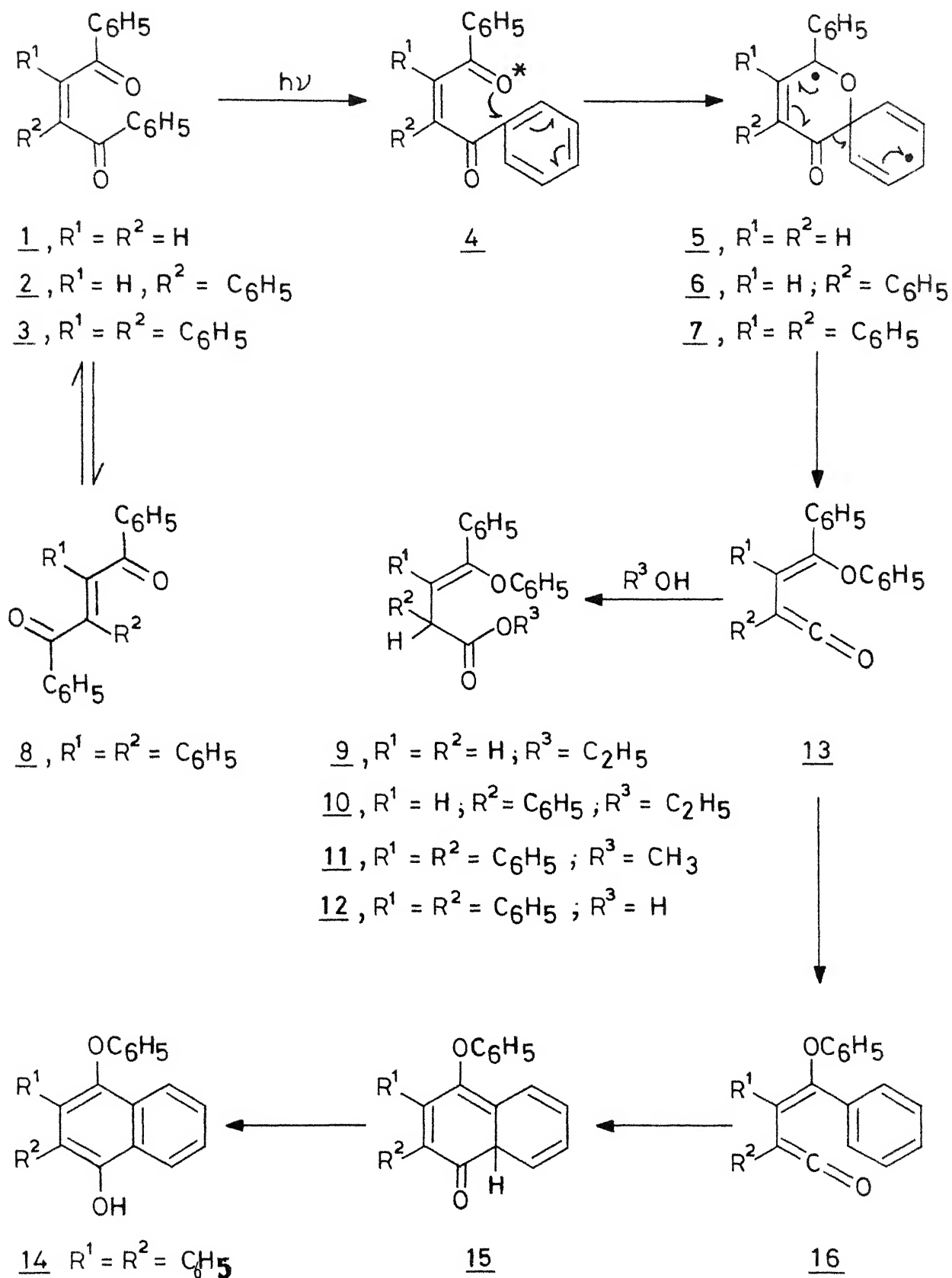
In continuation of our studies, we have examined the thermal transformations of 25 and 26. Heating of 25 around 370° for 1 hr resulted in the formation of a 26% yield of 2-endo-3-exo-dibenzoylbicyclo[2.2.1]heptane (44), presumably arising through a disproportionation reaction. In contrast, the thermolysis of 26 around 310° resulted in the formation of a 42% yield of 2-benzoyl-3-phenylbicyclo[2.2.2]oct-2-ene (47), which may arise through the decarbonylation of the lactonic intermediate 38.

Reasonable mechanisms have been suggested for the formation of the different products in the photochemical and thermal transformations of 25 and 26.

I.2 INTRODUCTION

Griffin and O'Connell¹ and also Zimmerman and co-workers² have shown that dibenzoylethylenes 1-3 undergo an interesting photorearrangement in protic solvents such as alcohols, resulting in the formation of the corresponding esters 9-11 (Scheme I.1). Thus, it has been observed that the photolysis of cis-1,2-dibenzoylethylene (1) in ethanol leads to the formation of ethyl 4-phenyl-4-phenoxy-3-butenate (9). Similar transformations have been observed in the case of dibenzoylstyrene (2) and dibenzoylstilbene (3), leading to the

Scheme I.1



formation of the corresponding esters 10 and 11, respectively. Padwa et al.³ have shown that the photolysis of trans-dibenzoylstilbene (8) gives rise to different products, depending upon the nature of the solvent employed. Thus, the irradiation of 8 in benzene, for example, gives a mixture of products consisting of cis-dibenzoylstilbene (3) and 1-hydroxy-2,3-diphenyl-4-phenoxy-naphthalene (14), whereas 2,3,4-triphenyl-4-phenoxy-3-butenic acid (12) is formed in aqueous dioxane. Mention may also be made that Sugiyama and Kashima⁴ have observed that the photolysis of 1,2-dibenzoyl-ethylene (1) in acidic methanol results in the formation of a mixture of products consisting of methyl 4-phenyl-4-phenoxy-3-butenate, 1,2-dibenzoyl-1-methoxyethane and 2,5-diphenylfuran.

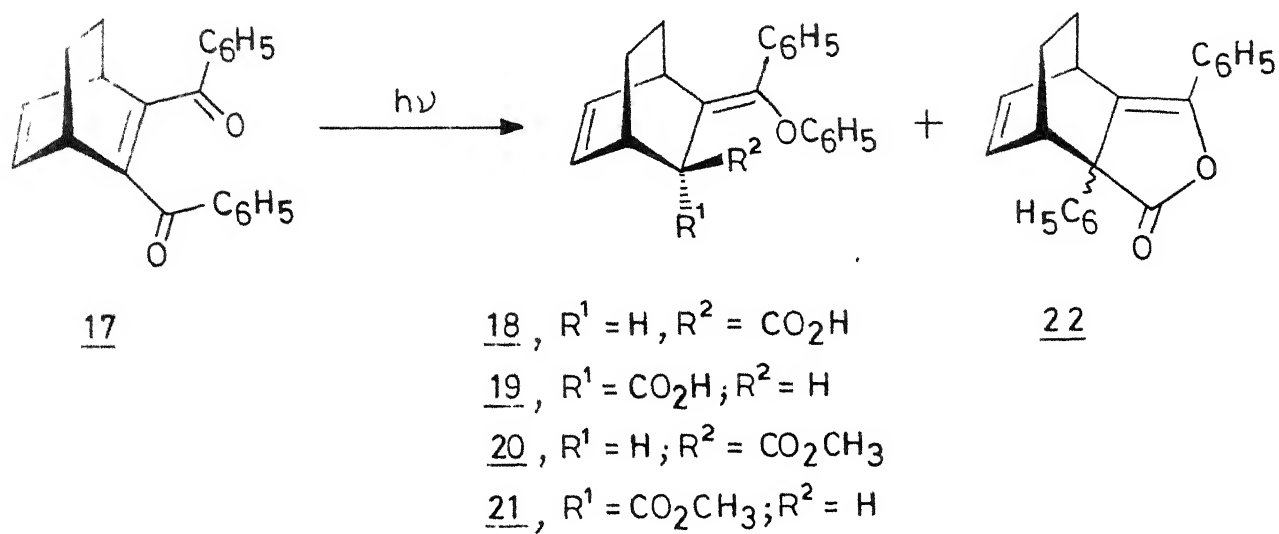
Zimmerman and co-workers⁵ had suggested that the phototransformations of dibenzoyl-ethylenes 1-3, giving rise to the corresponding esters 9-11, can be rationalized in terms of the pathway shown in Scheme I.1. On the basis of detailed quenching studies, they had suggested that the phototransformations of dibenzoyl-ethylenes proceed primarily from their excited singlet states.

In the photoreactions of dibenzoylalkenes, it has been generally observed that a major photochemical pathway involves the cis-trans isomerization of the alkene double bond. In recent studies,^{6,7} however, it has been shown that

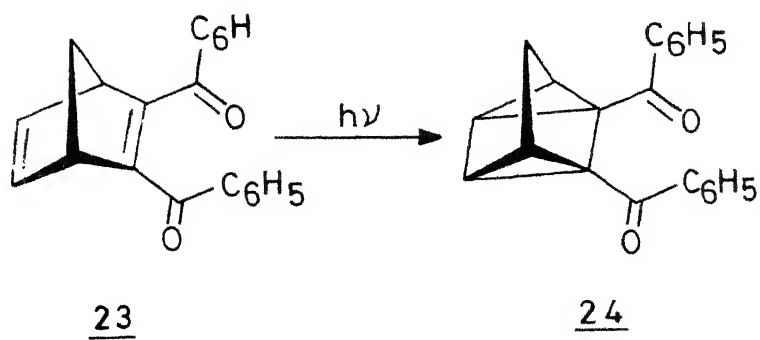
substrates, wherein the cis-trans isomerization possibility is prevented through geometric constraints, undergo the expected photorearrangement almost exclusively. Thus, it has been observed that the photolysis of a cis-1,2-dibenzoylalkene system such as 2,3-dibenzoylbicyclo[2.2.2]octa-2,5-diene (17) in benzene, for example, gives rise to a mixture of 6-(phenoxyphenylmethylene)bicyclo[2.2.2]oct-2-ene-5-exo-carboxylic acid (18, 26%), 6-(phenoxyphenylmethylene)-bicyclo[2.2.2]oct-2-ene-5-endo-carboxylic acid (19, 6%), and an isomeric lactone, 22 (23%) (Scheme I.2). The photolysis of 17 in methanol, on the other hand, has been reported to give a mixture of methyl 6-(phenoxyphenylmethylene)bicyclo[2.2.2]oct-2-ene-5-exo-carboxylate (20, 69%) and methyl 6-(phenoxyphenylmethylene)bicyclo[2.2.2]oct-2-ene-5-endo-carboxylate (21, 1%) (Scheme I.2). In contrast, the photo-transformation of 2,3-dibenzoylbicyclo[2.2.1]hept-2-ene (23) gave mostly 2,3-dibenzoylquadricyclo[2.2.1.0^{2,6}.0^{3,5}]heptane (24, 90%), presumably, arising through a $[\pi^2s + \pi^2s]$ type of photoaddition reaction (Scheme I.3).

The object of the present investigation has been to study the photochemical transformations of a few representative cis-1,2-dibenzoylalkene systems such as 2,3-dibenzoylbicyclo[2.2.1]hept-2-ene (25) and 2,3-dibenzoylbicyclo[2.2.2]oct-2-ene (26), wherein both the cis-trans isomerization of the alkene double bond and also the $[\pi^2s + \pi^2s]$ type of addition possibilities are absent.

Scheme I.2



Scheme I.3

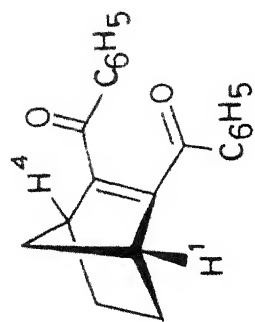


I.3 RESULTS AND DISCUSSION

I.3.1 Photolysis of cis-1,2-Dibenzoylalkenes

The cis-1,2-dibenzoylalkenes that we have employed in the present investigations, namely, 2,3-dibenzoylbicyclo[2.2.1]hept-2-ene (25) and 2,3-dibenzoylbicyclo[2.2.2]oct-2-ene (26) have been prepared from the corresponding diene precursors through catalytic hydrogenation. Thus, the catalytic hydrogenation of 2,3-dibenzoylbicyclo[2.2.1]hepta-2,5-diene (27) over 5% Pd on CaCO₃ in ethyl acetate gave a 93% yield of 2,3-dibenzoylbicyclo[2.2.1]hept-2-ene (25). Similarly, the hydrogenation of 2,3-dibenzoylbicyclo[2.2.2]octa-2,5-diene (28), under analogous conditions, gave a 89% yield of 2,3-dibenzoylbicyclo[2.2.2]oct-2-ene (26). The structures of both 25 and 26 have been established on the basis of analytical results and spectral data. The ¹H NMR spectrum of 25 (Fig. I.1), for example, showed a singlet at δ 3.50 (2 H), due to the bridgehead protons, whereas the methylene protons appeared as a complex multiplet centred around δ 1.78 (2 H). In addition, the spectrum contained a complex multiplet centred around δ 7.18 (10 H), due to the aromatic protons.

The ¹H NMR spectrum of 26 (Fig. I.2) showed a doublet at δ 3.15 (2 H), due to the bridgehead protons, whereas the methylene protons appeared as two sets of



Aromatic
7.18

H¹, H⁴
3.50

Methylene
1.78

TMS

← PPM (δ)

Fig. I.1 ¹H NMR spectrum (90 MHz) of 25.

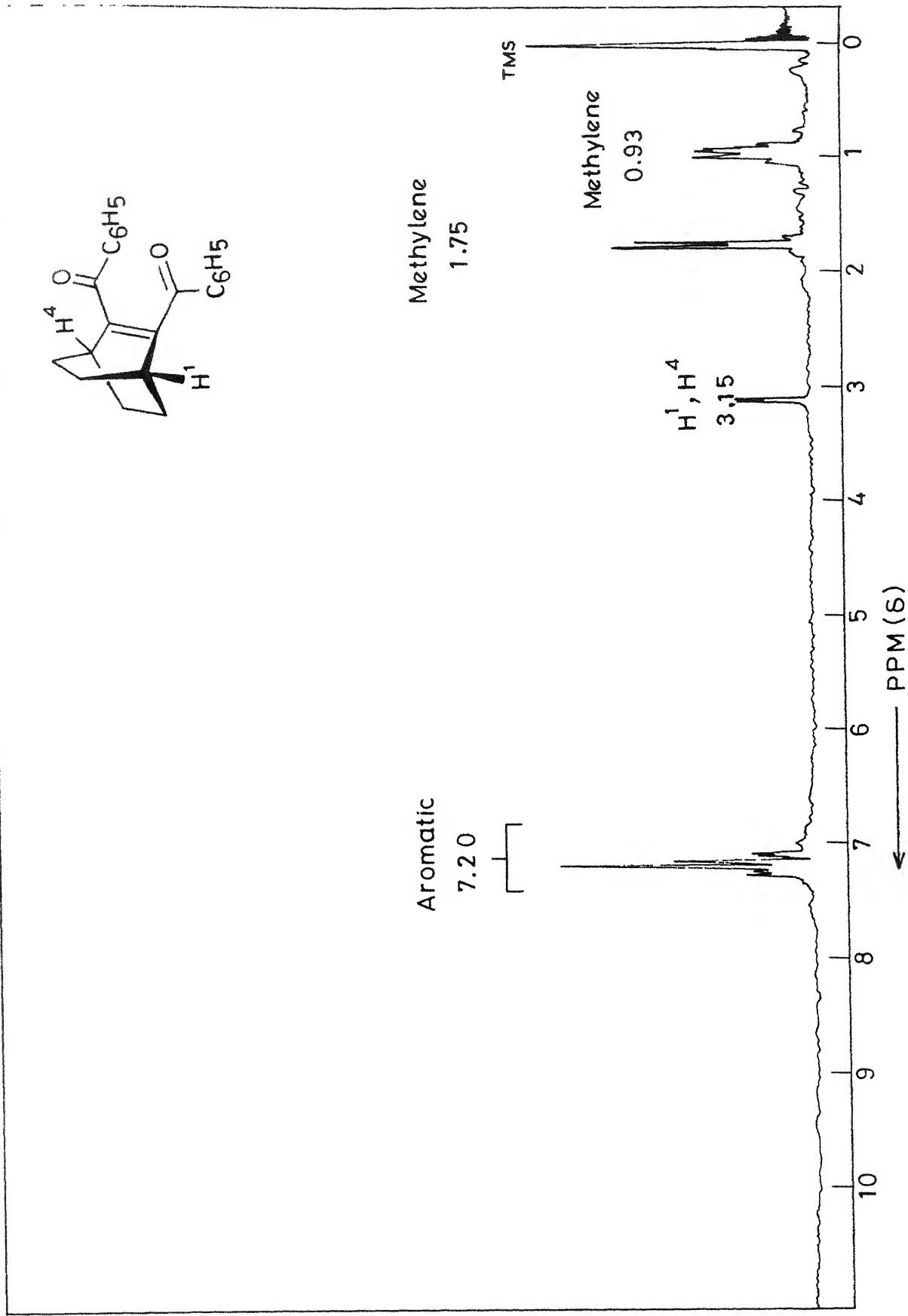


Fig. 1.2 ^1H NMR spectrum (270 MHz) of 26.

multiplets centred around δ 0.93 (4 H) and 1.75 (4 H), respectively. The aromatic protons appeared as a complex multiplet centred around δ 7.20 (10 H). Irradiation of a benzene solution of 2,3-dibenzoylbicyclo[2.2.1] hept-2-ene (25) gave a 15% yield of a product, identified as 3-(phenoxyphenylmethylene)bicyclo[2.2.1] heptane-2-exo-carboxylic acid (34), whereas in methanol, a 41% yield of methyl 3-(phenoxyphenylmethylene)bicyclo[2.2.1] heptane-2-exo-carboxylate (33) was obtained. The structures of 34 and 33 have been arrived at on the basis of analytical results and spectral data.

The ^1H NMR spectrum of 34 (Fig. I.3), for example, showed a complex multiplet centred around δ 1.75 (6 H), assigned to the methylene protons and two broad singlets at δ 2.66 (1 H) and 3.16 (1 H), respectively, assigned to the bridgehead protons. In addition, the spectrum displayed a doublet at δ 3.50 (1 H), with a coupling constant of 2.5 Hz, which has been assigned to the endo proton. The aromatic protons in 34 appeared as a complex multiplet centred around δ 7.01 (11 H).

The mass spectrum of 34 (Fig. I.4) showed a molecular ion peak at m/e 320. In addition, the spectrum showed several signals at m/e 293 (2), 275 (2), 247 (2), 226 (19), 199 (47), 198 (7), 171 (23), 170 (10), 167 (4), 166 (6), 165 (8),

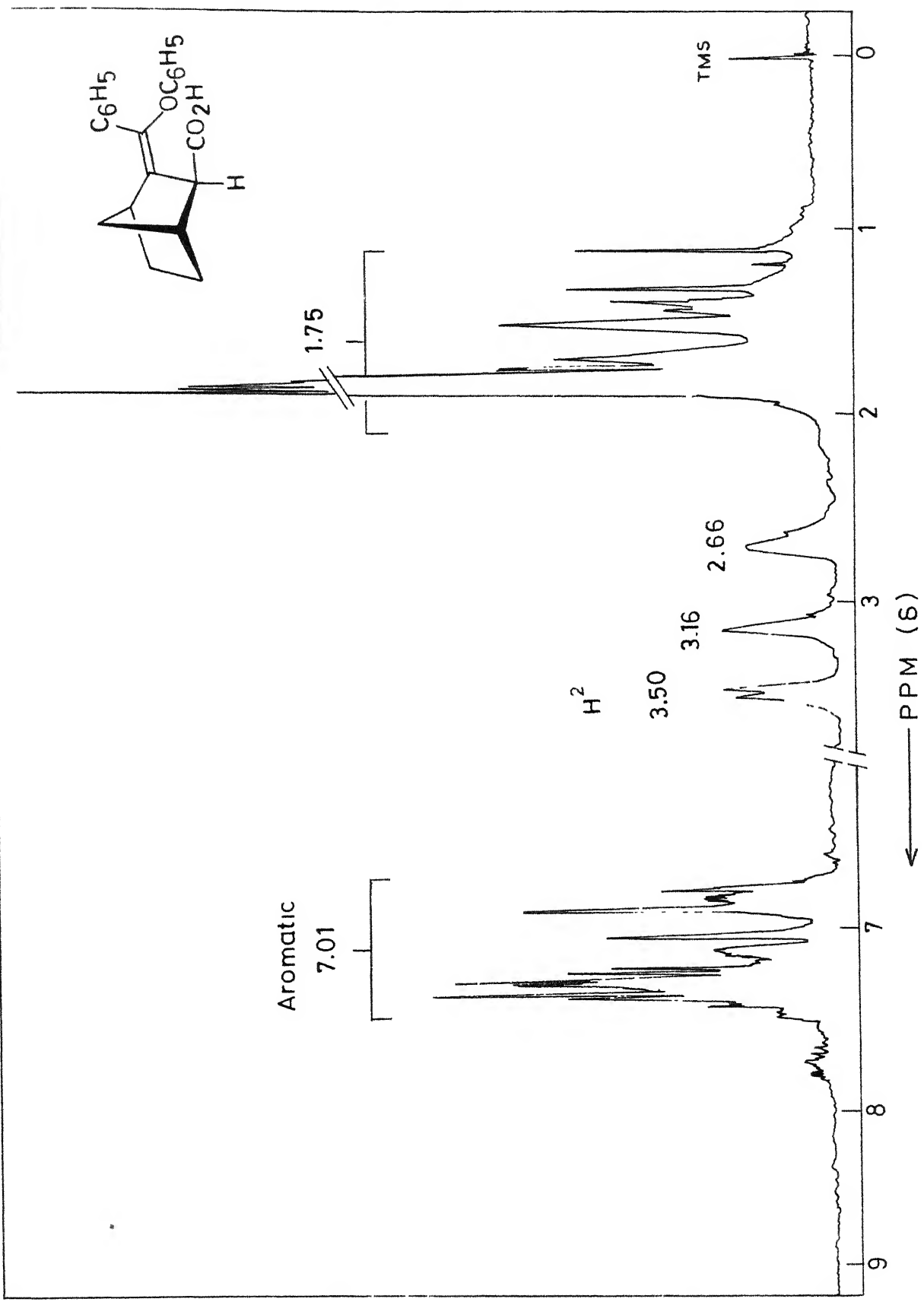


Fig. I.3 ^1H NMR spectrum (80 MHz) of 34.

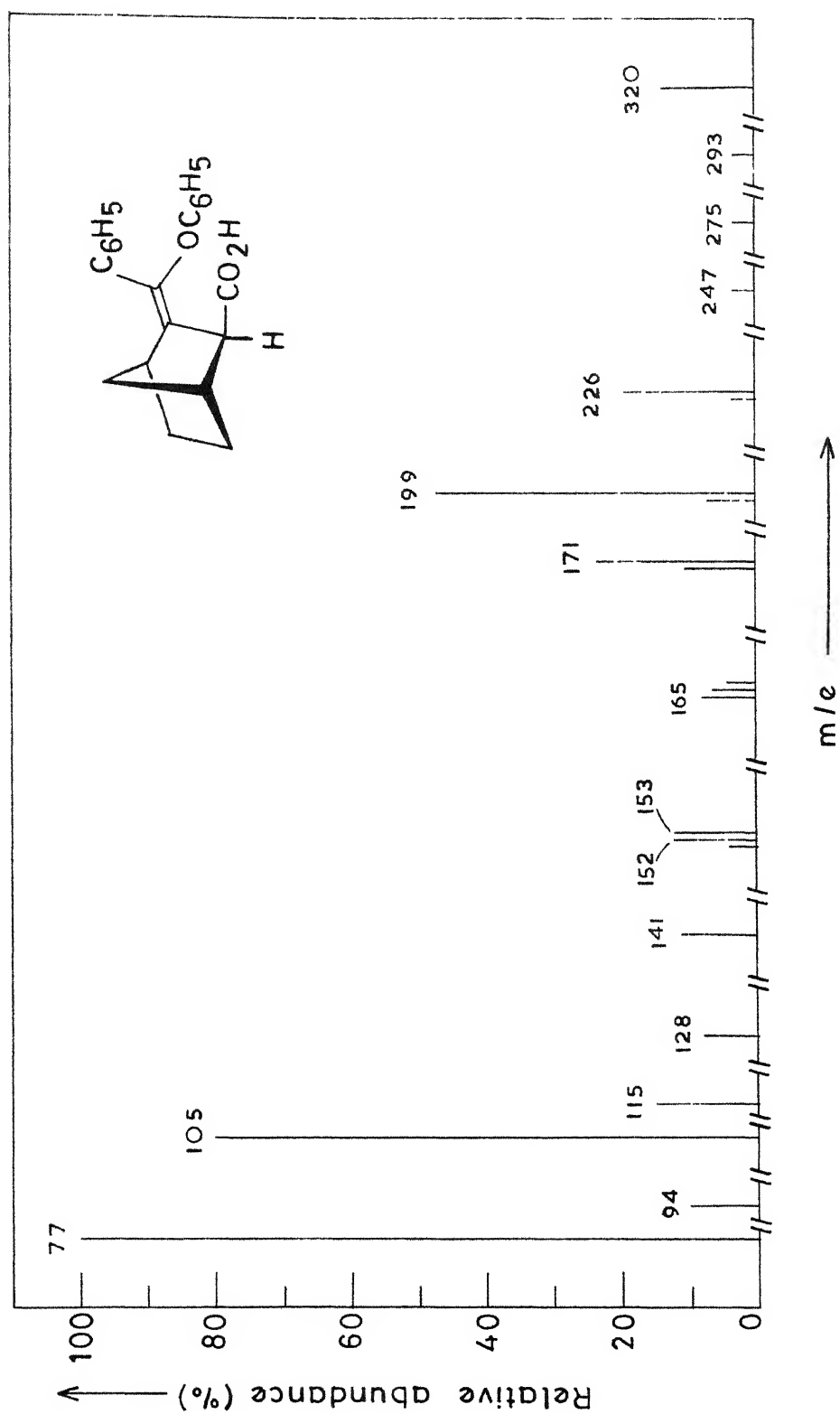
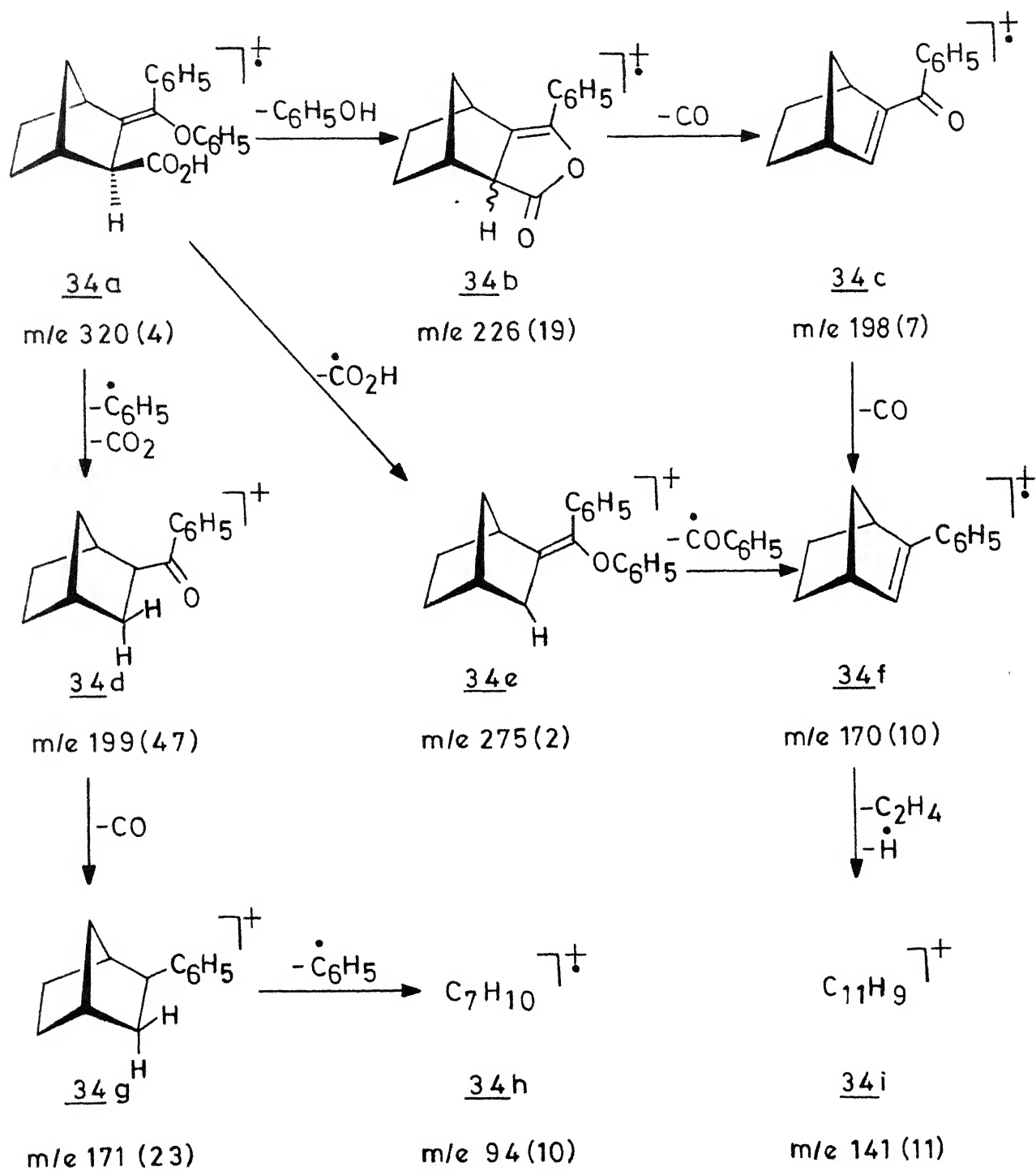


Fig. 1.4 Mass spectrum of $\underline{34}$.

153 (12), 152 (12), 151 (3), 141 (11), 128 (8), 115 (15), 105 (80), 94 (10), 77 (100) and 51 (8). Some of the possible fragmentations of 34 are shown in Scheme I.4. The loss of both phenyl and hydroxyl radicals from the molecular ion 34a will result in the fragment 34b at m/e 226. Further loss of carbon monoxide from 34b will result in 34c at m/e 198, which in turn can lose an additional CO to give the fragment 34f at m/e 170. The loss of a CO_2H fragment from the molecular ion, on the other hand, will give rise to the fragment 34e at m/e 275, whereas the loss of both C_6H_5 and CO_2 fragments from 34a will result in 34d at m/e 199, which in turn can lose CO to give 34g at m/e 171. The loss of a phenyl group from 34g will, however, result in 34h at m/e 94, whereas the loss of a C_2H_4 fragment and hydrogen atom from 34f will give 34i at m/e 141.

The ^1H NMR spectrum of 33 (Fig. I.5) showed a multiplet centred around δ 1.74 (6 H) due to the methylene protons and two singlets at δ 2.69 (1 H) and 3.14 (1 H), due to the bridgehead protons. The ester methyl group appeared as a singlet at δ 3.29 (3 H), whereas the endo proton appeared as a doublet at δ 3.62 ($J_{1,2} = 2.7$ Hz). The aromatic protons appeared as two sets of multiplets, centred around δ 6.82 (2 H) and 7.30 (8 H), respectively.

Scheme I.4



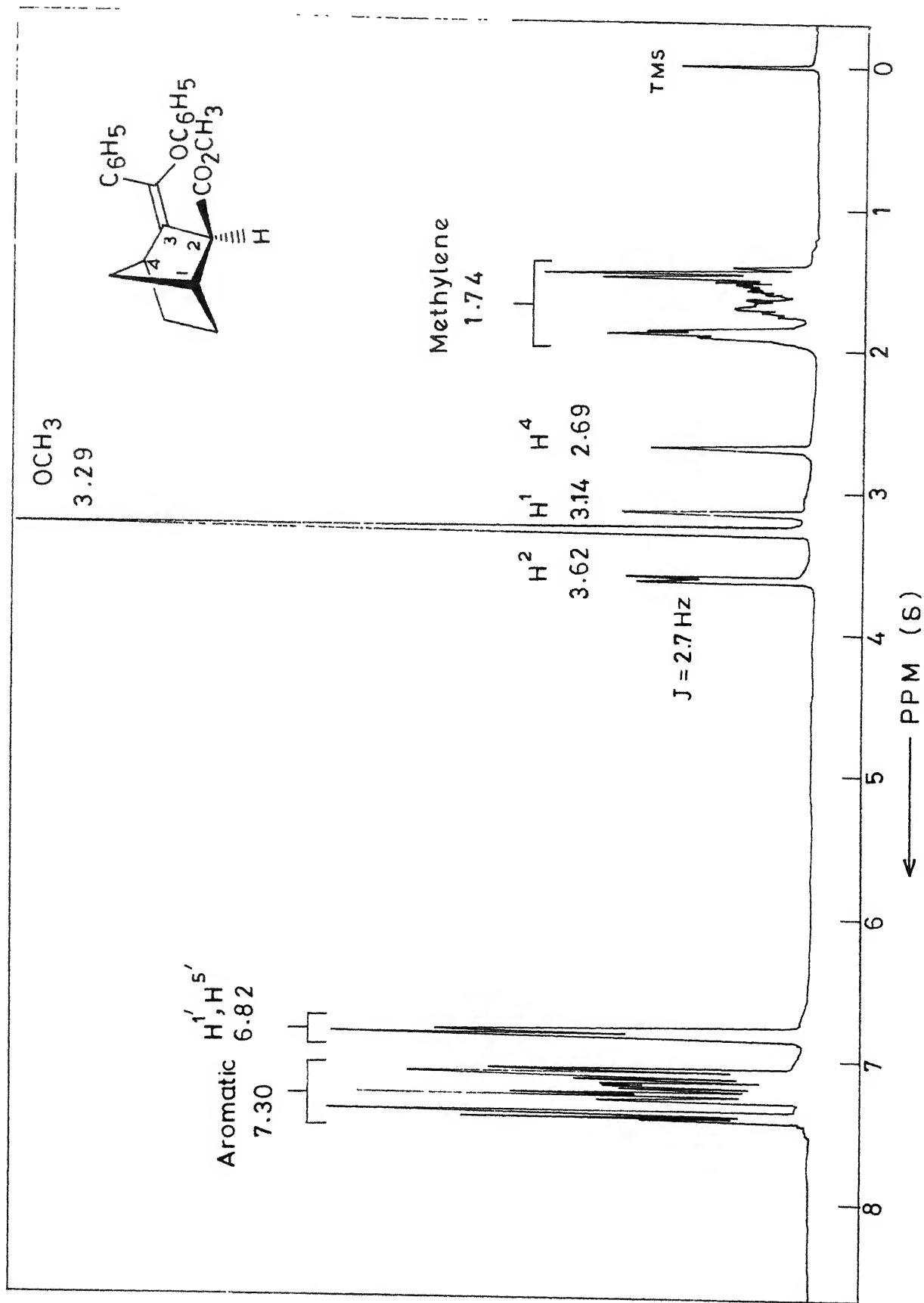


Fig. I.5 ^1H NMR spectrum (270 MHz) of 33.

The mass spectrum of 33 (Fig. I.6) showed the molecular ion peak at m/e 334 (25). In addition, the spectrum showed several peaks at m/e 302 (2), 275 (8), 247 (5), 243 (100), 185 (36), 181 (8), 165 (8), 153 (12), 152 (11), 141 (7), 128 (6), 115 (16), 105 (41), 77 (53), 65 (7) and 59 (14). Some of the fragmentation modes of the molecular ion 33a are shown in Scheme I.5.

The formation of products such as 33 and 34 in the photolysis of 25 can be rationalized in terms of the pathways shown in Scheme I.6. In this scheme, we assume that the initial step in the reaction is the excitation of 25, which eventually leads to its triplet state (25*). Subsequent interaction of one of the carbonyl groups in 25* with the π -system of an adjacent phenyl group will result in the diradical intermediate 31 (path 'a'), which in turn is transformed to the ketene intermediate 30, through pathways analogous to the phototransformations of dibenzoylethylenes.¹⁻⁵ The ketene intermediate 30 can subsequently react with moisture present in the solvent (benzene) to give the carboxylic acid 34 or with methanol to give the methyl ester 33 (Scheme I.6).

An alternative mode of transformation of 25* is through path 'b', shown in Scheme I.6. As per this route, 25* can interact with the π -system of the adjacent carbonyl

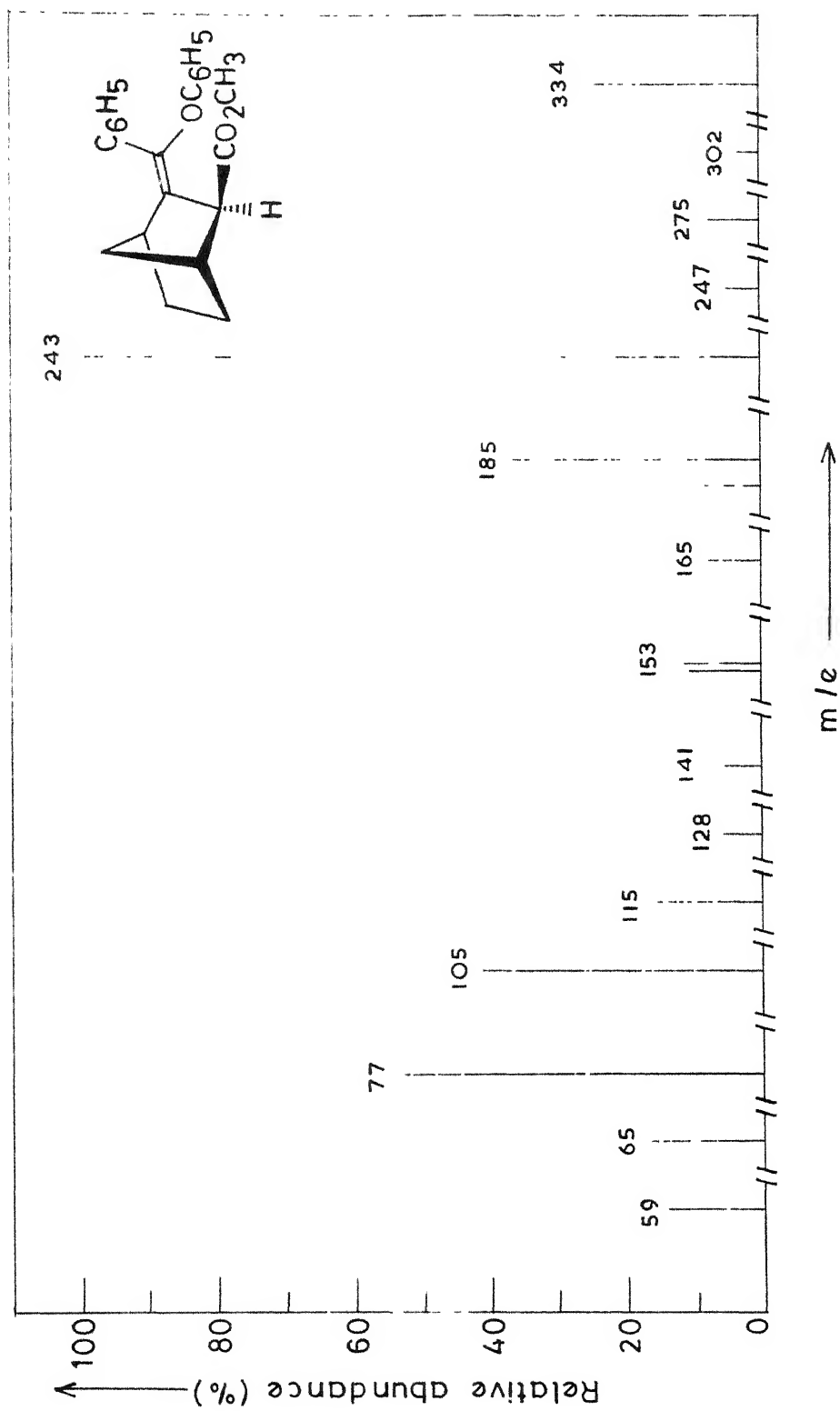
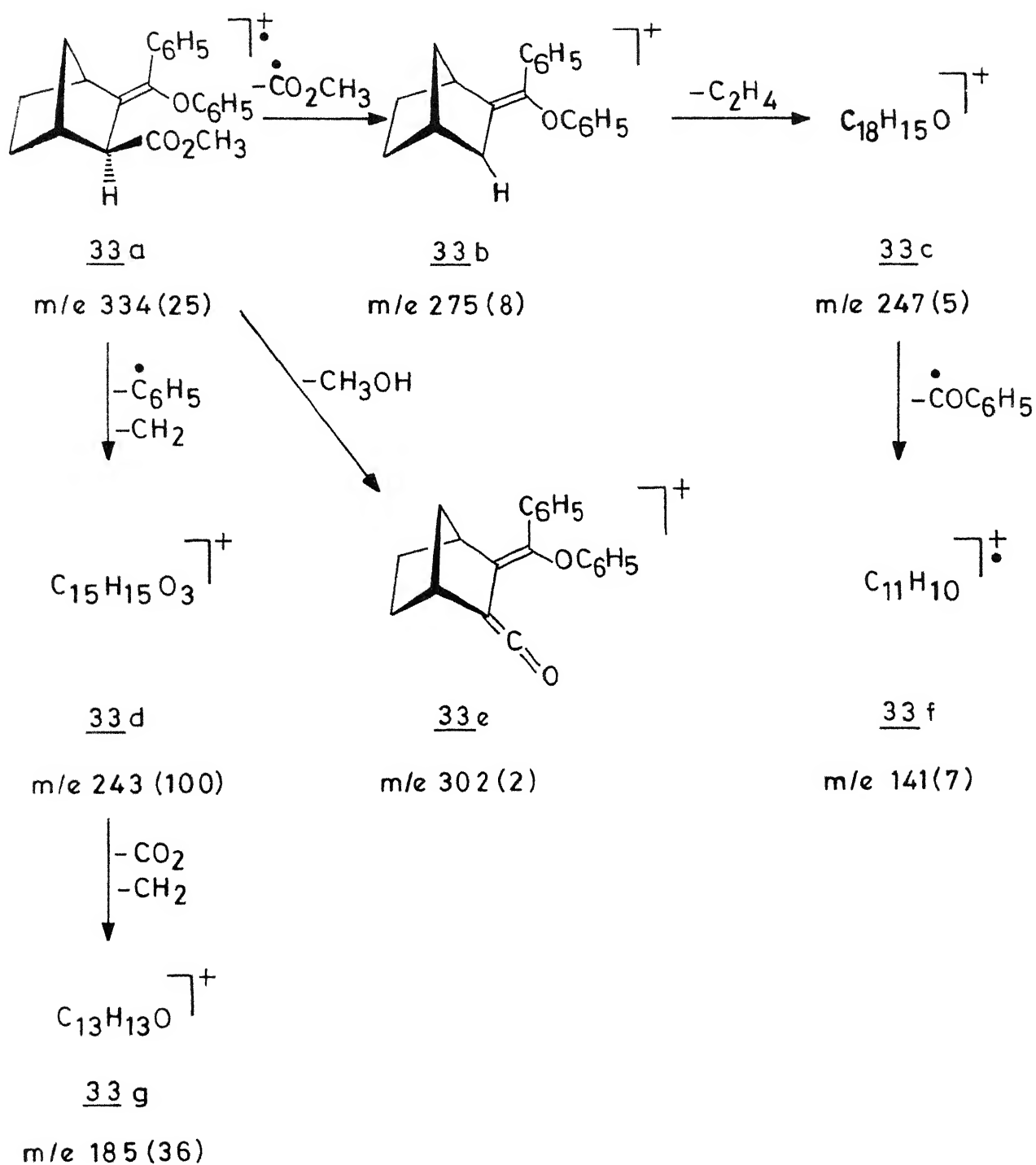
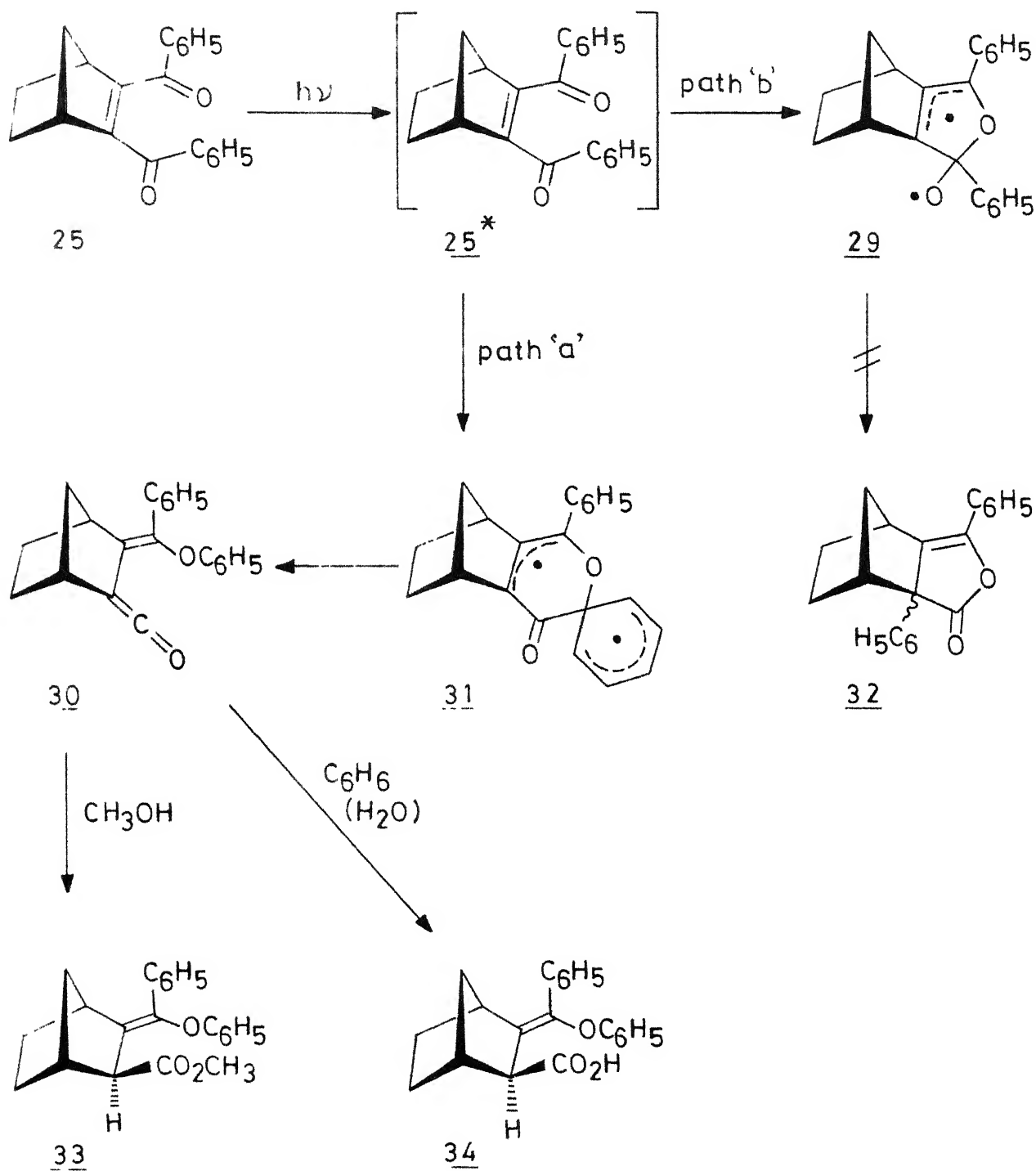


Fig. I.6 Mass spectrum of 33.

Scheme 1.5



Scheme I.6



group to give the diradical intermediate 29, which in turn can rearrange to the lactone 32. The fact that 32 is not observed in the phototransformations of 25 suggests that the diradical 31 is preferred over 29. It is not clear whether steric considerations are involved in directing the course of the photoreaction of 25 through the diradical intermediate 31, in any preferential manner.

Similarly, the irradiation of a benzene solution of 2,3-dibenzoylbicyclo[2.2.2]oct-2-ene (26) gave a mixture of products consisting of 3-(phenoxyphenylmethylene)bicyclo[2.2.2]octane-2-carboxylic acid (40, 7%) and the bicyclic lactone 38 (20%). On the other hand, when the irradiation of 26 was carried out in methanol, a 20% yield of methyl 3-(phenoxyphenylmethylene)bicyclo[2.2.2]octane-2-carboxylate (39) was obtained. The structures of the different photoproducts 38, 39 and 40 have been arrived at on the basis of analytical results and spectral data.

The ^1H NMR spectrum of the lactone 38 (Fig. I.7), for example, showed a complex multiplet centred around δ 1.70 (8 H), due to the methylene protons and two singlets at δ 2.78 (1 H) and 3.0 (1 H), due to the bridgehead protons. In addition, the spectrum showed a complex multiplet centred around δ 7.35 (10 H) due to the aromatic protons.

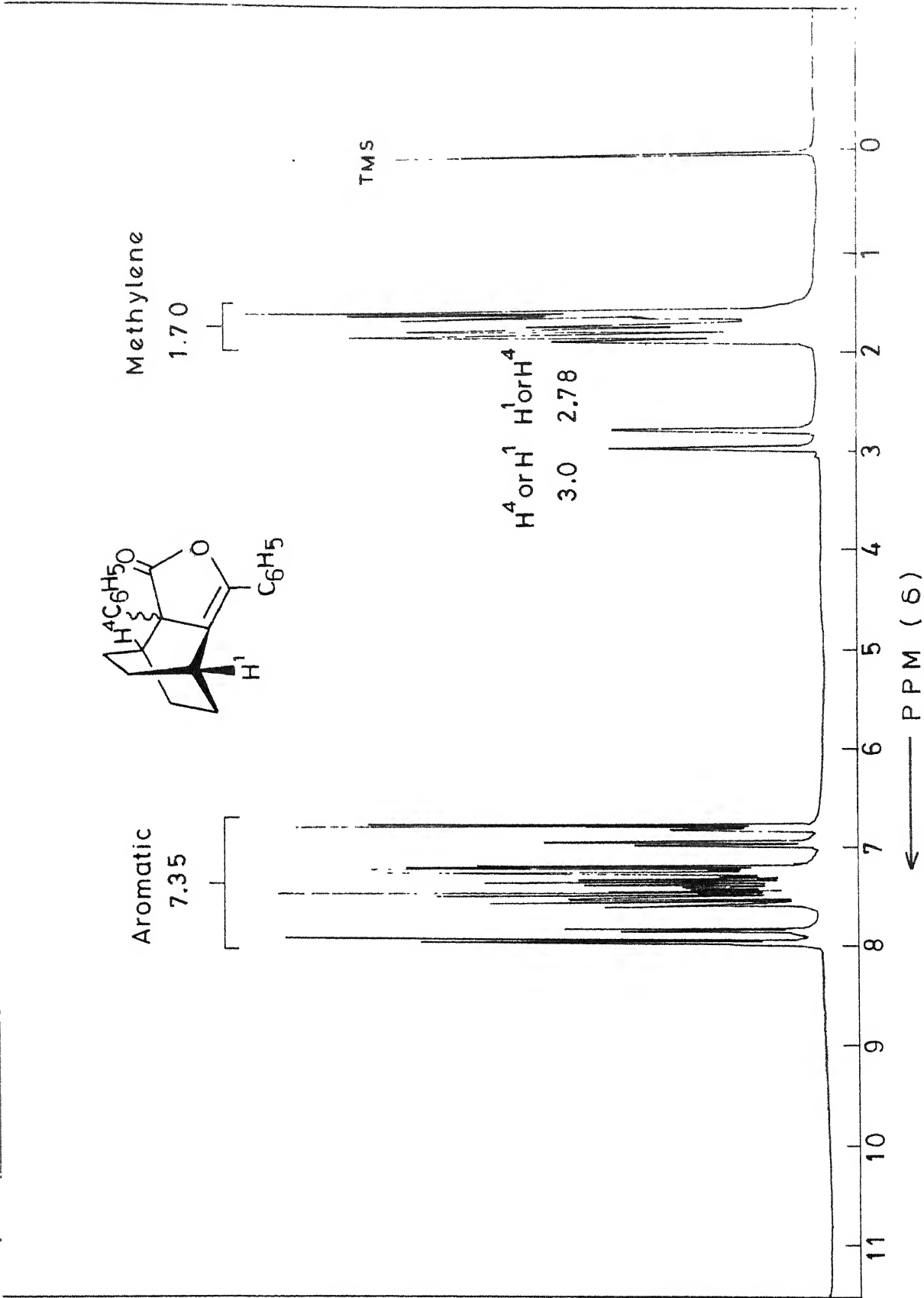


Fig. 1.7 NMR spectrum (270 MHz) of 38.

The mass spectrum of 38 (Fig. I.8) showed a molecular ion peak at m/e 316 (14). Other peaks in the spectrum were observed at m/e 288 (1), 240 (5), 239 (23), 222 (1), 221 (1), 211 (11), 209 (3), 194 (3), 193 (2), 182 (2), 166 (1), 165 (6), 156 (1), 154 (1), 153 (1), 152 (1), 115 (3), 105 (44), 32 (22) and 28 (100). Some of the probable fragmentation modes, which are in tune with the assigned structure 38, are shown in Scheme I.7.

The ^1H NMR spectrum of methyl 3-(phenoxyphenyl-methylene)bicyclo[2.2.2]octane-2-carboxylate (39) (Fig. I.9) showed a multiplet centred around δ 1.6 (8 H) due to the methylene protons and two other multiplets, centred around δ 2.0 (1 H) and 2.70 (1 H), respectively, due to the bridgehead protons. In addition, the spectrum showed a singlet at δ 3.4 (3 H), due to the ester methoxy protons and superimposed on this singlet was a multiplet centred around δ 3.4 (1 H), assigned to the methine proton, attached to the carbon, bearing the ester group. The aromatic protons appeared as a complex multiplet centred around δ 7.0 (10 H).

The mass spectrum of 39 (Fig. I.10) showed a molecular ion peak at m/e 348 (2). In addition, the spectrum showed several peaks at m/e 304 (2), 303 (9), 256 (99), 255 (100), 228 (2), 227 (52), 211 (20), 199 (5), 162 (5), 134 (8), 133 (12), 106 (6), 105 (26), 91 (26),

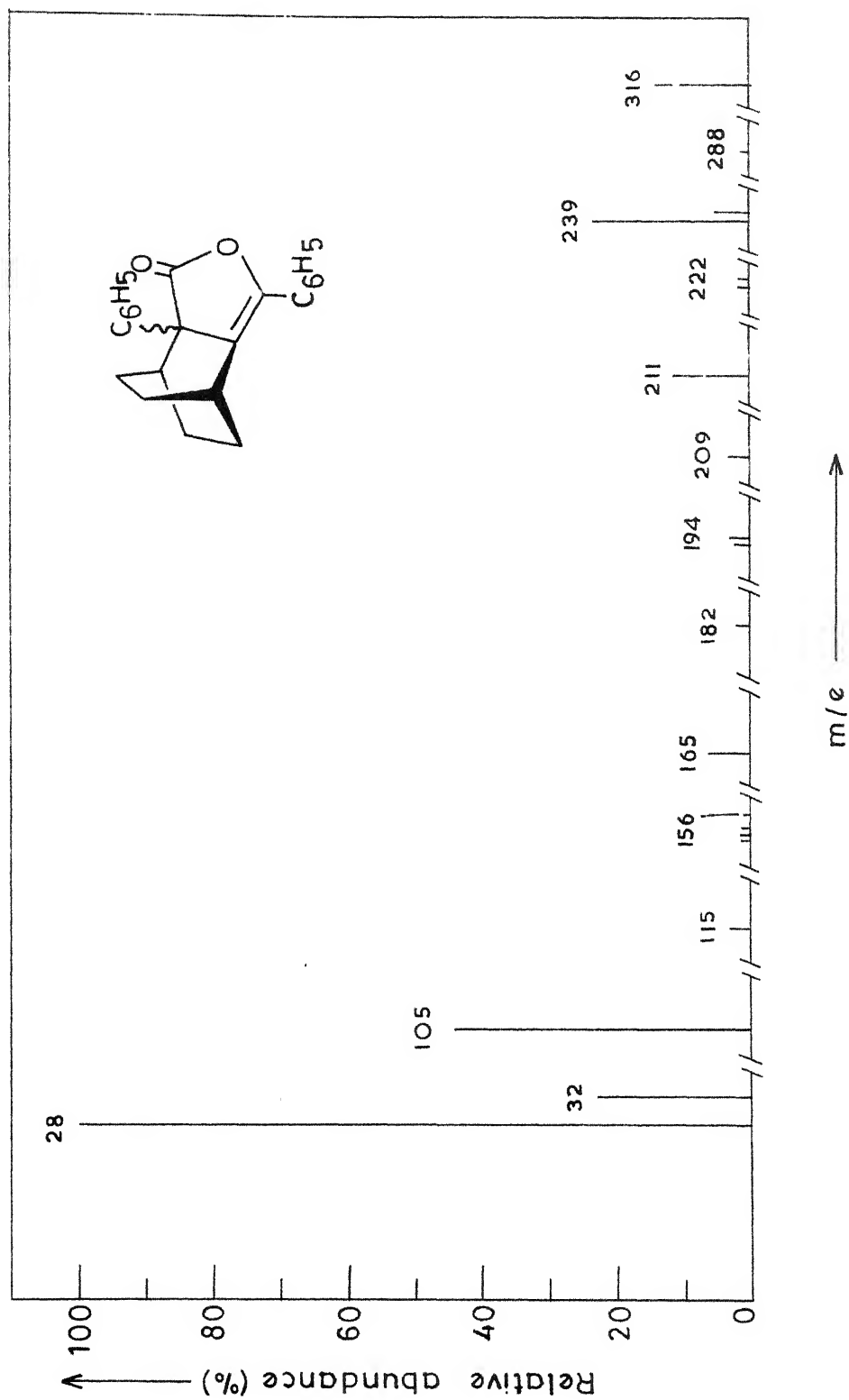
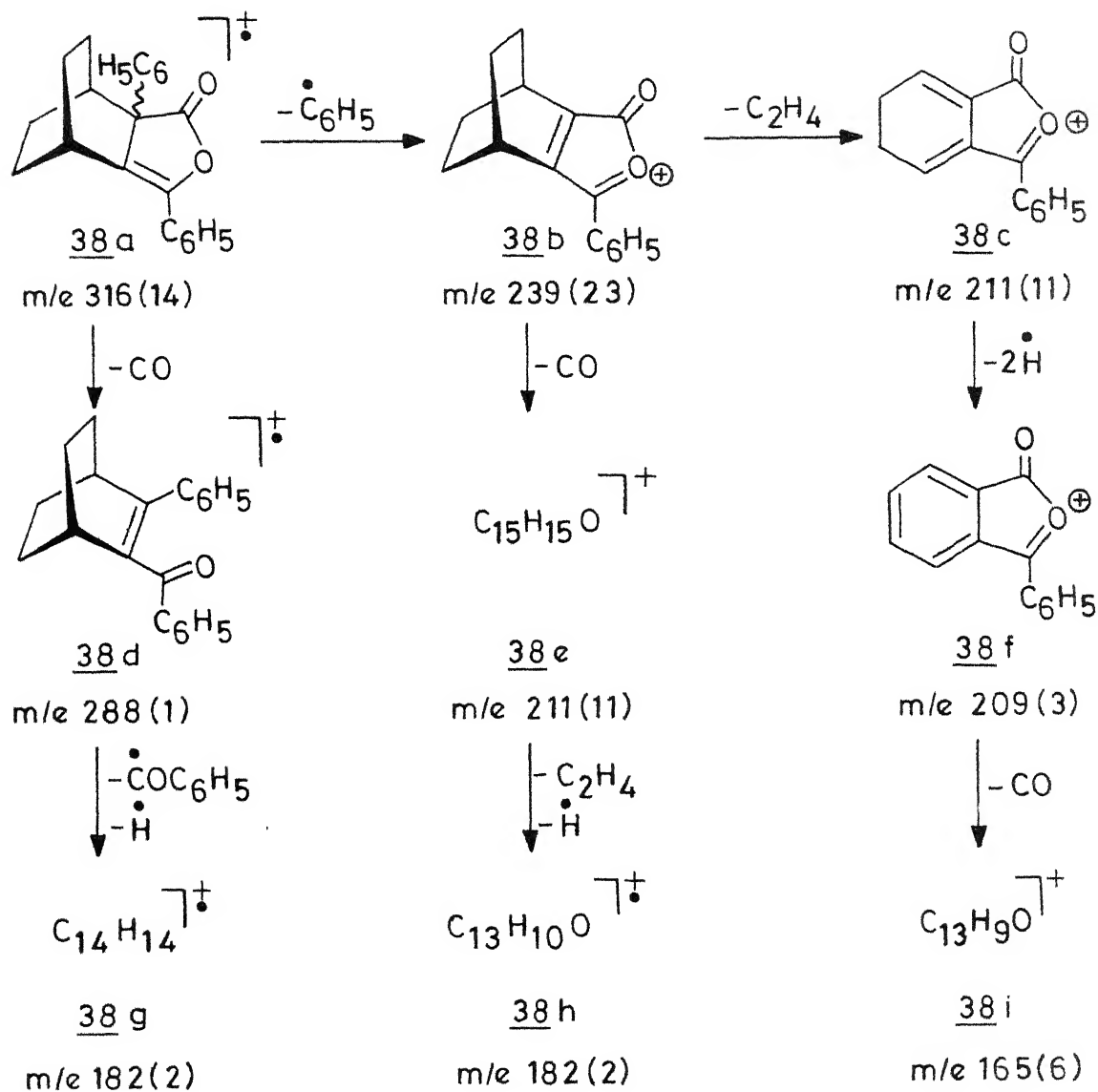


Fig. 1.8 Mass spectrum of 38.

Scheme 1.7



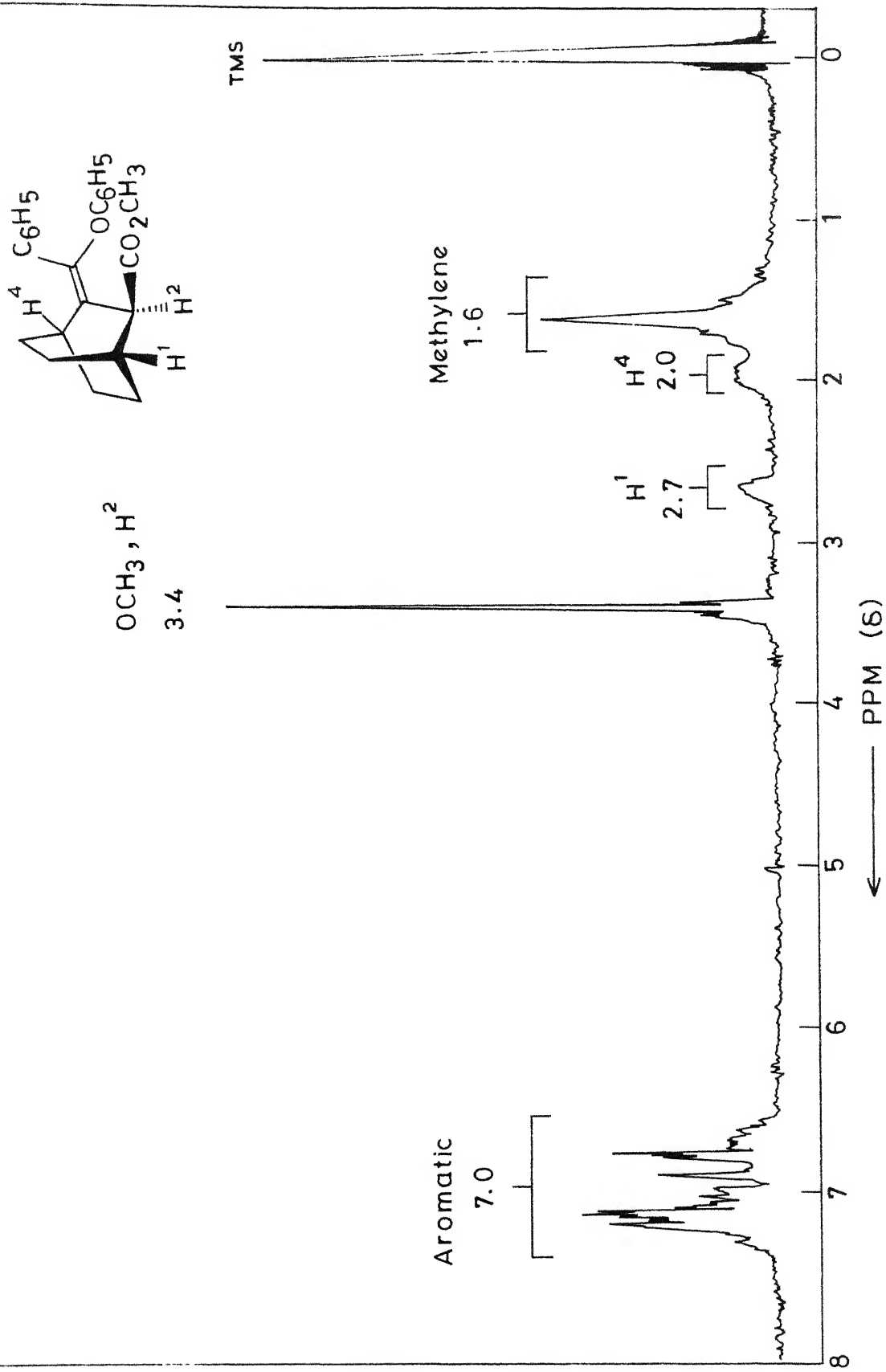


Fig. I.9 ^1H NMR spectrum (60 MHz) of 39.

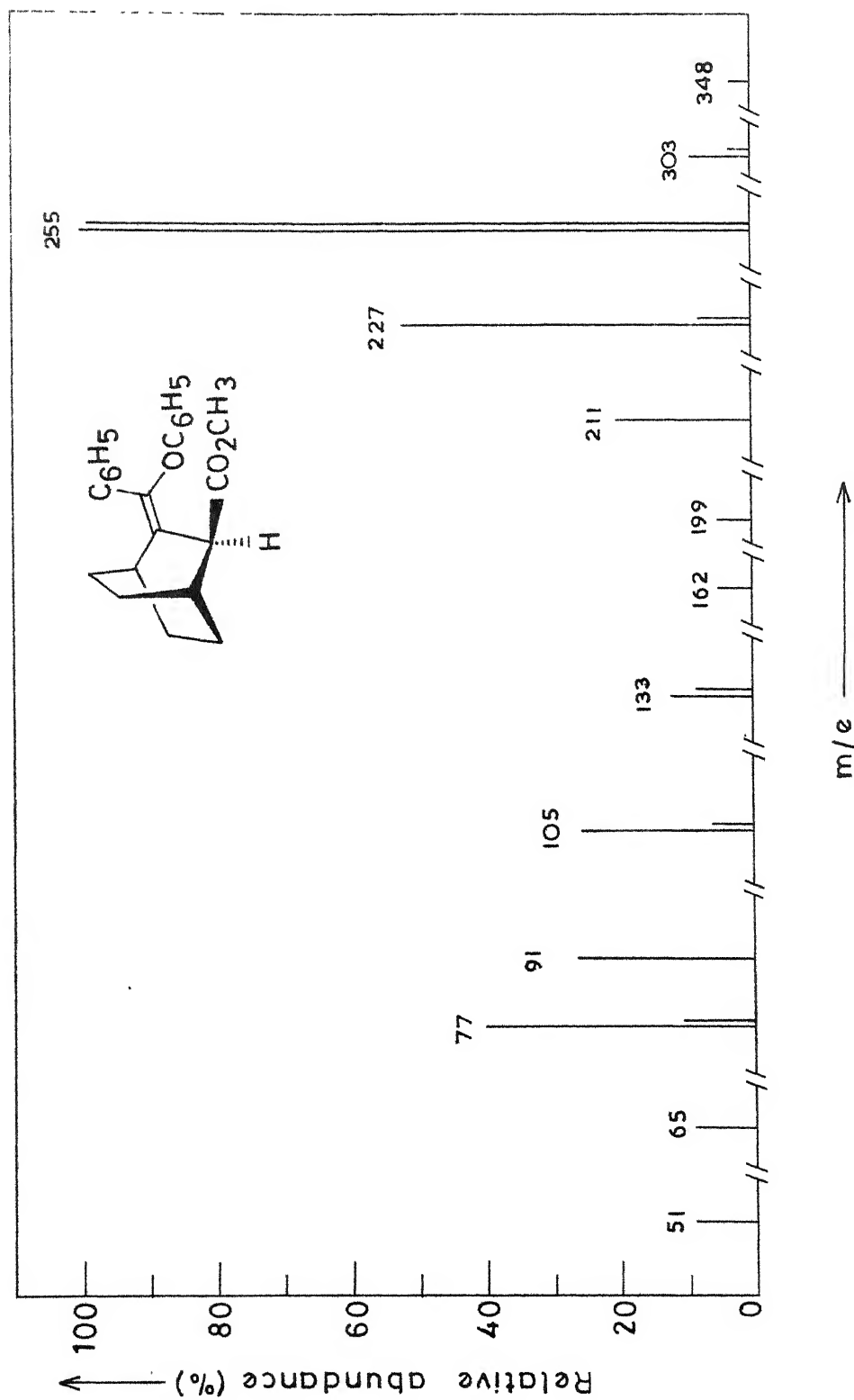


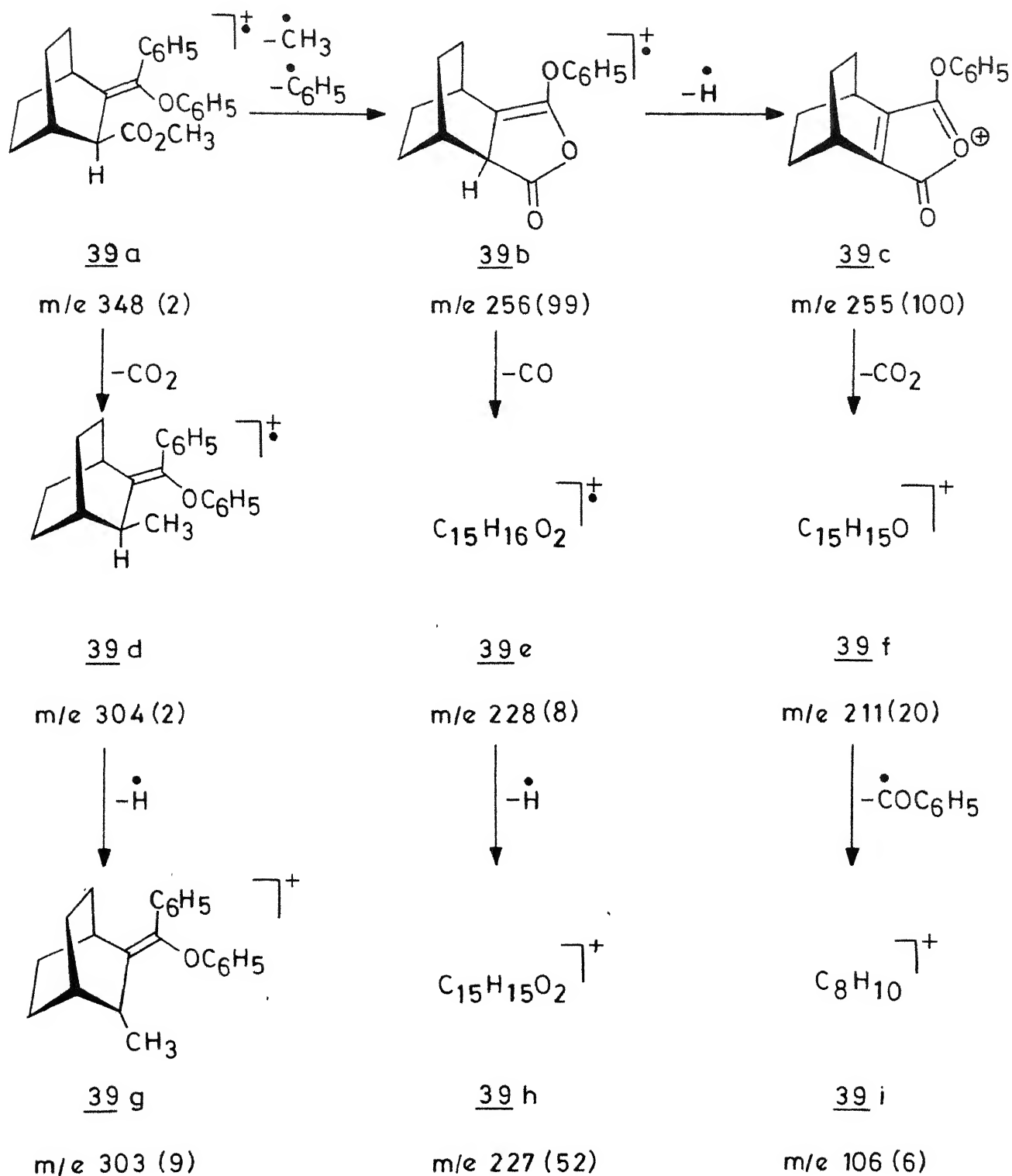
Fig. I.10 Mass spectrum of 39.

78 (11), 77 (40), 65 (9) and 51 (9). Some of the probable fragmentation patterns are shown in Scheme I.8.

The mass spectrum of 3-(phenoxyphenylmethylene)-bicyclo[2.2.2]octane-2-carboxylic acid (40) (Fig. I.11) showed a molecular ion peak at m/e 334 (50). In addition, the spectrum showed several peaks at m/e 315 (1), 290 (4), 289 (18), 241 (9), 240 (43), 239 (9), 213 (50), 212 (19), 211 (10), 197 (5), 196 (10), 195 (12), 185 (9), 184 (30), 183 (19), 168 (19), 167 (25), 166 (18), 165 (24), 155 (19), 153 (23), 152 (30), 135 (14), 129 (16), 128 (20), 117 (12), 115 (37), 105 (77), 77 (100), 65 (23) and 57 (12). Some of the likely fragmentation pathways for the molecular ion 40a are shown in Scheme I.9.

The correlation between the ester 39 and the acid 40 has been established through the base-catalyzed hydrolysis of 39, wherein a 63% yield of the acid 40 was isolated.

The formation of products such as 38, 39 and 40 in the photolysis of 26 can be rationalized in terms of the pathways shown in Scheme I.10. It is assumed that the initial step in the reaction involves the excitation of 26 to its excited singlet state, which undergoes rapid inter-system crossing to give the excited triplet state 26*. Subsequent interaction of one of the carbonyl groups with the π -system of an adjacent phenyl ring will result in the

Scheme 1.8

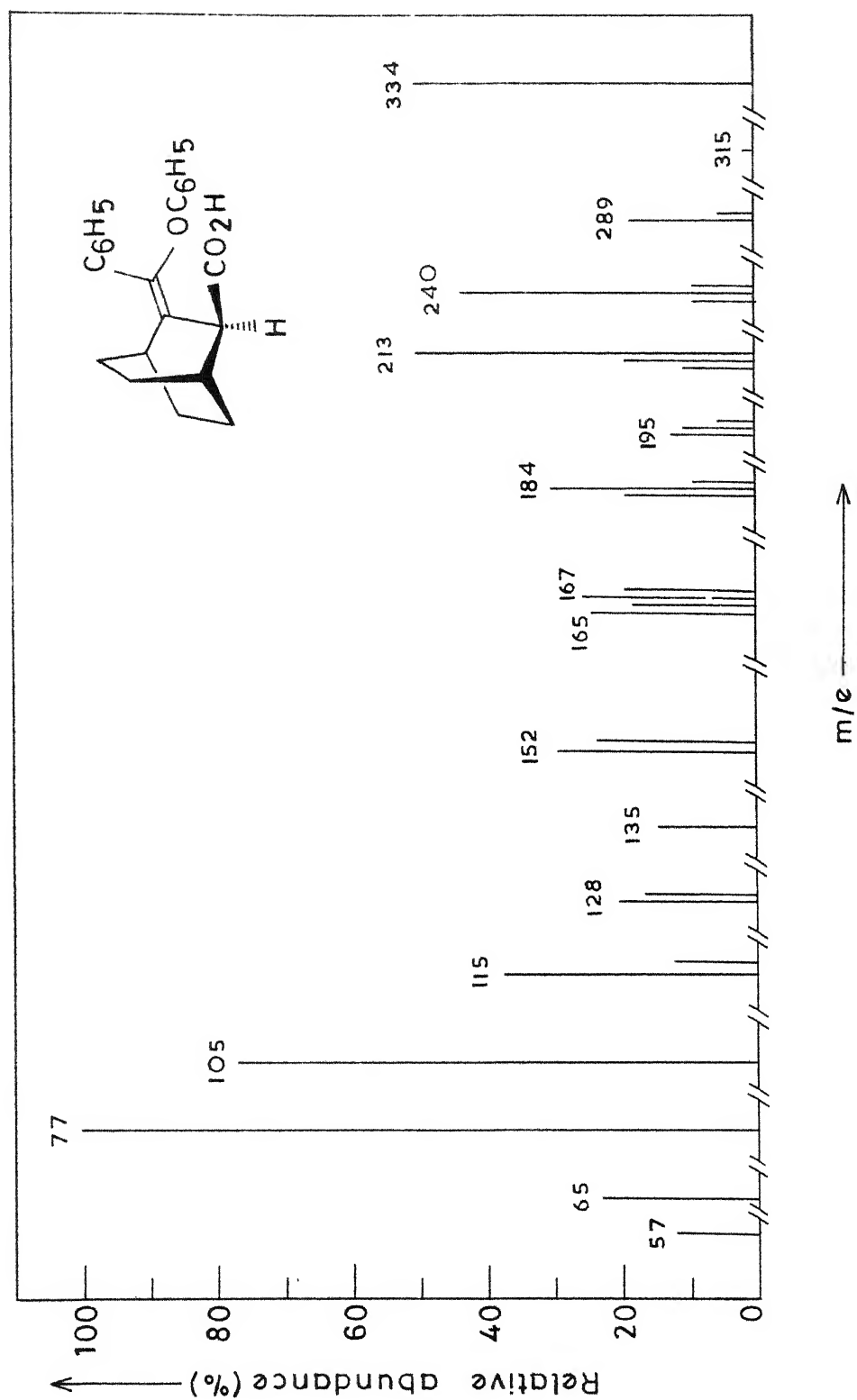
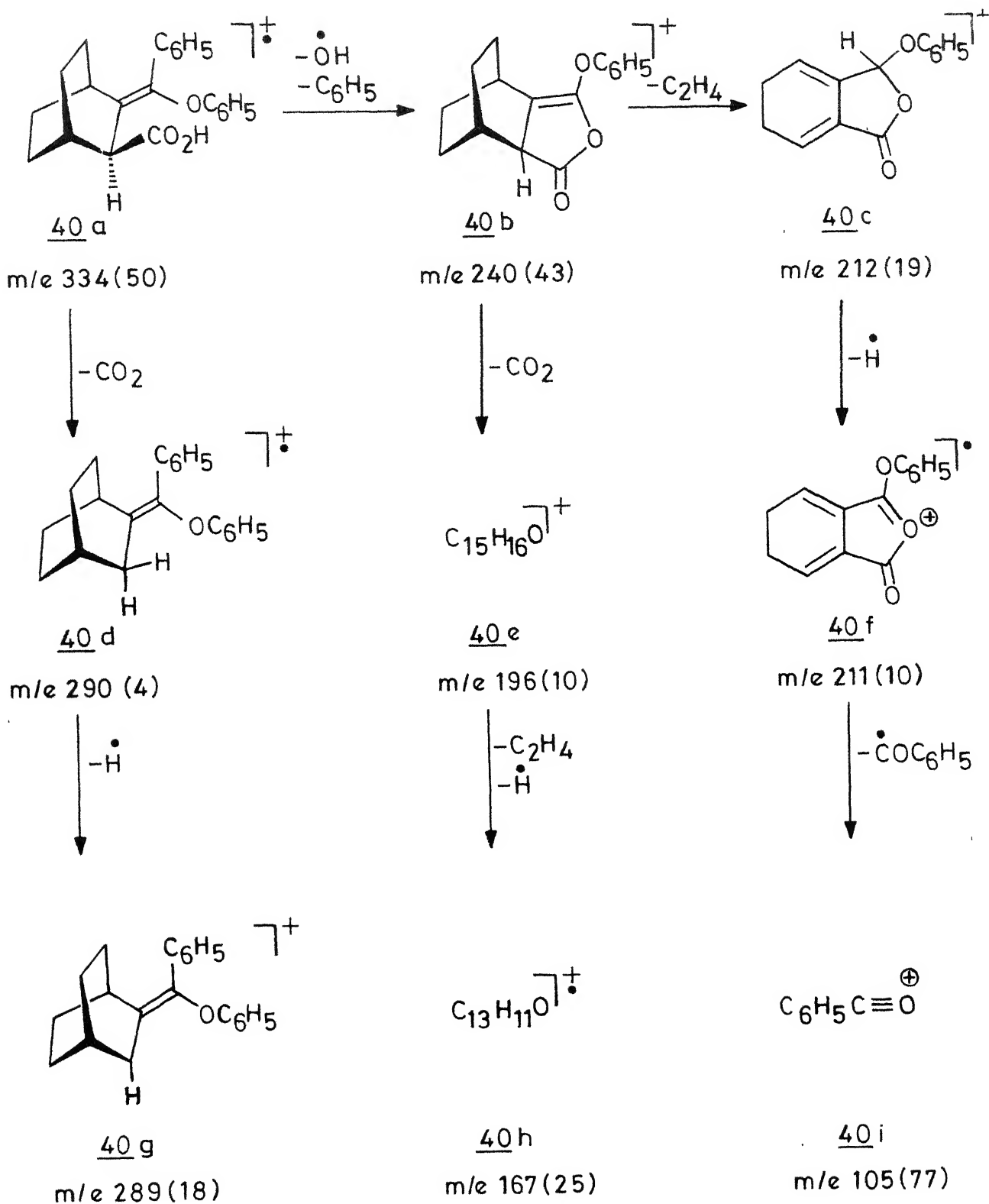
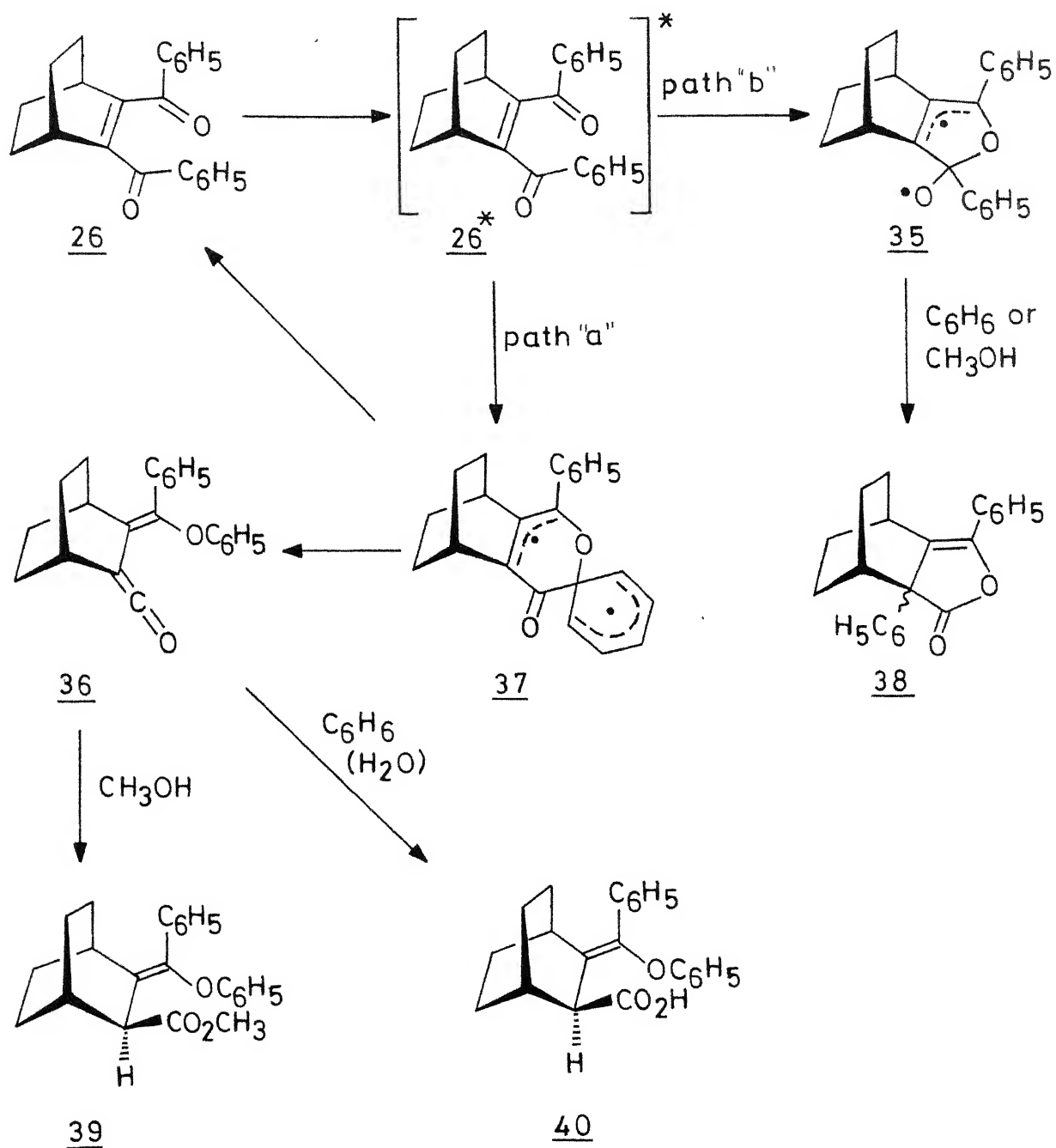


Fig. I.11 Mass spectrum of 40.

Scheme I.9



Scheme I.10



formation of the diradical intermediate 37 (path 'a'), which in turn will be transformed to the ketene 36. The ketene intermediate 36, can subsequently react with moisture present in the solvent (benzene) to give the carboxylic acid 40 or with methanol to give the ester 39.

An alternative mode of transformation of 26* will be to give rise to the diradical 35, arising through the interaction between the two carbonyl groups (path 'b'), which can subsequently rearrange to the lactone 38. The fact that the lactone 38 has been observed in the photo-transformation of a rigid cis-dibenzoylalkene system such as 26 would indicate that this is a possible pathway for the transformation of dibenzoylethylenes, in which the cis-trans isomerization mode is prevented. It may be mentioned in this connection that similar photorearrangements of cis-1,2-dibenzoylalkene derivatives, leading to the corresponding lactonic products have been observed in the case of tetrabenzoylethylene⁹ and also 6,7-dibenzoyl-tricyclo[3.3.2.0^{2,3}]nona-6,8-diene.¹⁰

I.3.2 Laser Flash-Photolysis Studies

With a view to gaining some insight into the mechanism of the phototransformations of cis-1,2-dibenzoylalkenes such as 2,3-dibenzoylbicyclo[2.2.1]hept-2-ene (25) and 2,3-dibenzoylbicyclo[2.2.2]oct-2-ene (26) and also to understand the type of

intermediates involved in these reactions, we have carried out the laser flash-photolysis studies of these two substrates.¹¹ Laser excitations were carried out under oxygen-free conditions, with pulses (337.1 nm, 8 ns, 3 mJ) from a nitrogen laser.

Laser excitation of a methanol solution of 26, for example, led to intense transient signals with $\lambda_{\text{max}} \sim 440$ nm and a lifetime (monitored at 430 nm) of 16 ± 2 μ s. This transient has been found to decay into a new species of rather similar spectrum, with $\lambda_{\text{max}} \sim 410$ nm and the lifetime of this species was long enough to be beyond the resolution of the instrument employed and therefore was estimated to exceed 50 μ s. In several cases it had been observed that the first two or three points did not fit well with the rest of the data on the decay curve, suggesting thereby, that an even shorter lived transient may be involved.

It has been assumed that this shorter lived species could be the triplet state 26*, whereas the short-lived transient could be attributed to one of the biradical species 37 or 35 (Scheme I.10). This biradical species has been found to interact with oxygen and di-tert-butyl nitroxide and the rate constants for these processes in methanol have been measured to be 5.7×10^8 and $1.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, respectively. It might be mentioned in this connection that triplet-derived biradicals are known to react with paramagnetic reagents.¹²⁻¹⁴

The long-lived transient may probably be assigned to the ketene intermediate 36. If the two transients observed are on the same reaction pathway, then the short lived biradical may be represented by 37 (Scheme I.10).

It has also been observed that the triplet state of phenanthrene is efficiently quenched by 26 with a rate constant of $\sim 10^9 \text{ M}^{-1} \text{ s}^{-1}$ and that the quenching process leads to the formation of the same transients as in the direct-irradiation experiments.

The quantum yield for the consumption of 26 has been measured gas chromatographically and it was found to be, $\phi = 0.04$. It is pertinent to observe that the transient signals observed on laser excitation of 26 have been quite intense and clearly cannot be attributed to species generated with a low quantum yield. It appears therefore, that the diradical species 37, formed with higher quantum yields undergoes reconversion to the starting material 26.

In the case of 2,3-dibenzoylbicyclo[2.2.1] hept-2-ene (25), however, it has been observed that the transient spectra are less intense than those observed in the case of 26 and that short- and long-lived intermediates overlap extensively in the visible region of the spectrum. It has been found that the short-lived species has a lifetime of 3 μs and that it interacts

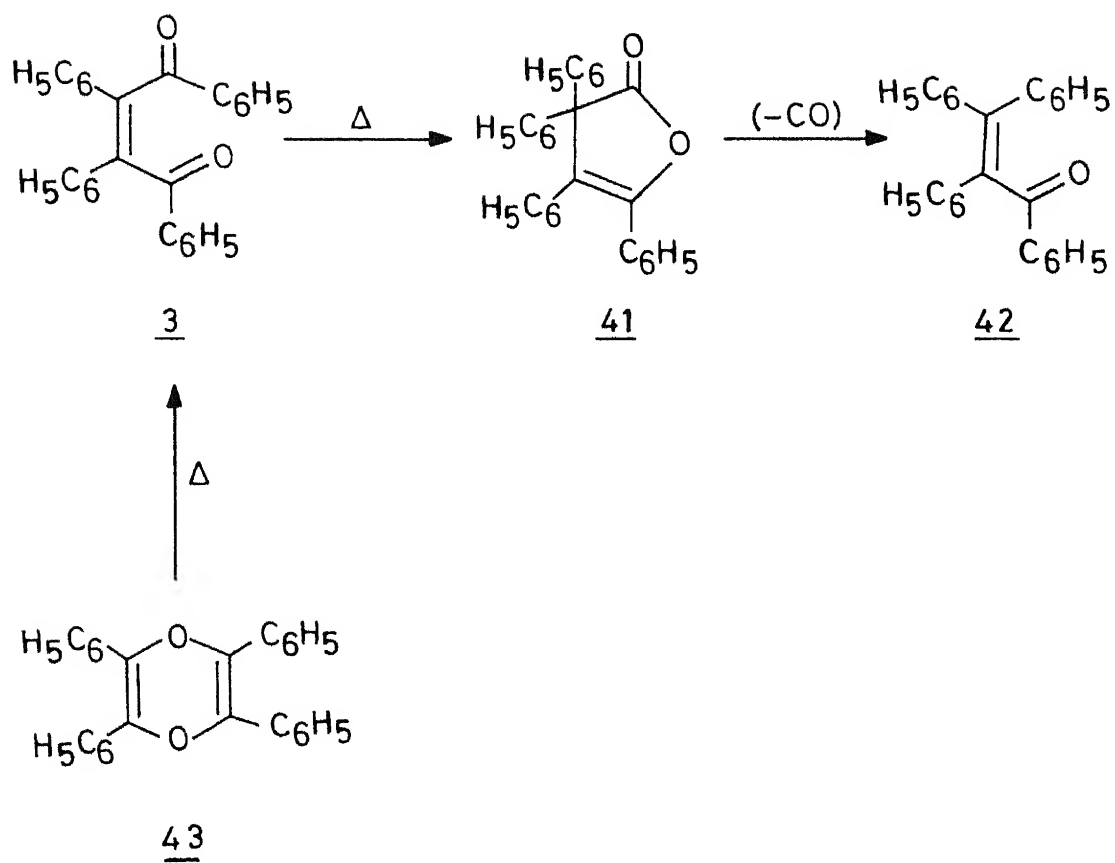
with O_2 with $k = 7 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, with di-tert-butyl nitroxide with $k = 1.7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ and with a typical triplet quencher, 2,5-dimethyl-2,4-hexadiene with $k = 7 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$. Also, it has been observed that 25 quenches phenanthrene triplets with $k_q \simeq 2.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ and that phenanthrene-sensitization leads to transient phenomena similar to those observed in the direct irradiations. The quantum yield of consumption of 25 has been found to be, $\phi = 0.02$.

The laser flash-photolysis studies, thus, reveal that a diradical intermediate such as 31 may be involved in the phototransformations of 25, leading to the different products, as shown in Scheme I.6.

I.3.3 Thermal Transformations of a Few cis-1,2-Dibenzoylalkenes

Several examples of the thermal transformations of cis-1,2-dibenzoylalkenes are reported in the literature.¹⁵⁻²¹ Zinin, for example, had reported that the thermolysis of cis-1,2-dibenzoylstilbene (3) leads to an isomeric lactone 41.¹⁵ Subsequent studies by Japp and Klingemann¹⁶ have shown that the product isolated by Zinin in the thermolysis of 3 is actually the decarbonylated derivative 42 and not the isomeric lactone 41 (Scheme I.11).

Scheme I.11



It may be mentioned in this connection that, the reported thermal rearrangement of tetraphenyl-*p*-dioxin (43) to give the lactone 41,¹⁷ has been shown to involve cis-1,2-dibenzoylstilbene as an intermediate which then undergoes further transformation to give the lactone 41.^{18,20}

In the present studies, we have examined the thermal transformations of both 2,3-dibenzoylbicyclo[2.2.1]hept-2-ene (25) and 2,3-dibenzoylbicyclo[2.2.2]oct-2-ene (26), with a view to understanding the nature of the products formed in these reactions. Heating of 25 around 310° for 1 hr, for example, gave a 26% yield of a product, identified as 2-endo-3-exo-dibenzoylbicyclo[2.2.1] heptane (44). The structure of 44 has been arrived at on the basis of analytical results and spectral data. Further, it has been shown that 44 is formed in a 69% yield, when 27 is hydrogenated over 5% Pd on CaCO₃.

The ¹H NMR spectrum of 44 (Fig. I.12), for example, showed several signals at δ 1.29 (m, 2 H), 1.67 (m, 2 H), 1.80 (d, 1 H), 2.56 (s, 1 H), 2.76 (s, 1 H), 4.14 (d, 1 H), 4.49 (m, 1 H), 7.50 (m, 6 H) and 8.04 (m, 4 H). Of these, the multiplets at δ 1.29 and 1.67 were assigned to the methylene protons, whereas the doublet at δ 1.80 with a coupling constant of 10 Hz ($J_{7,7'}$) was assigned to the H-7' proton. It may be mentioned in this connection that the

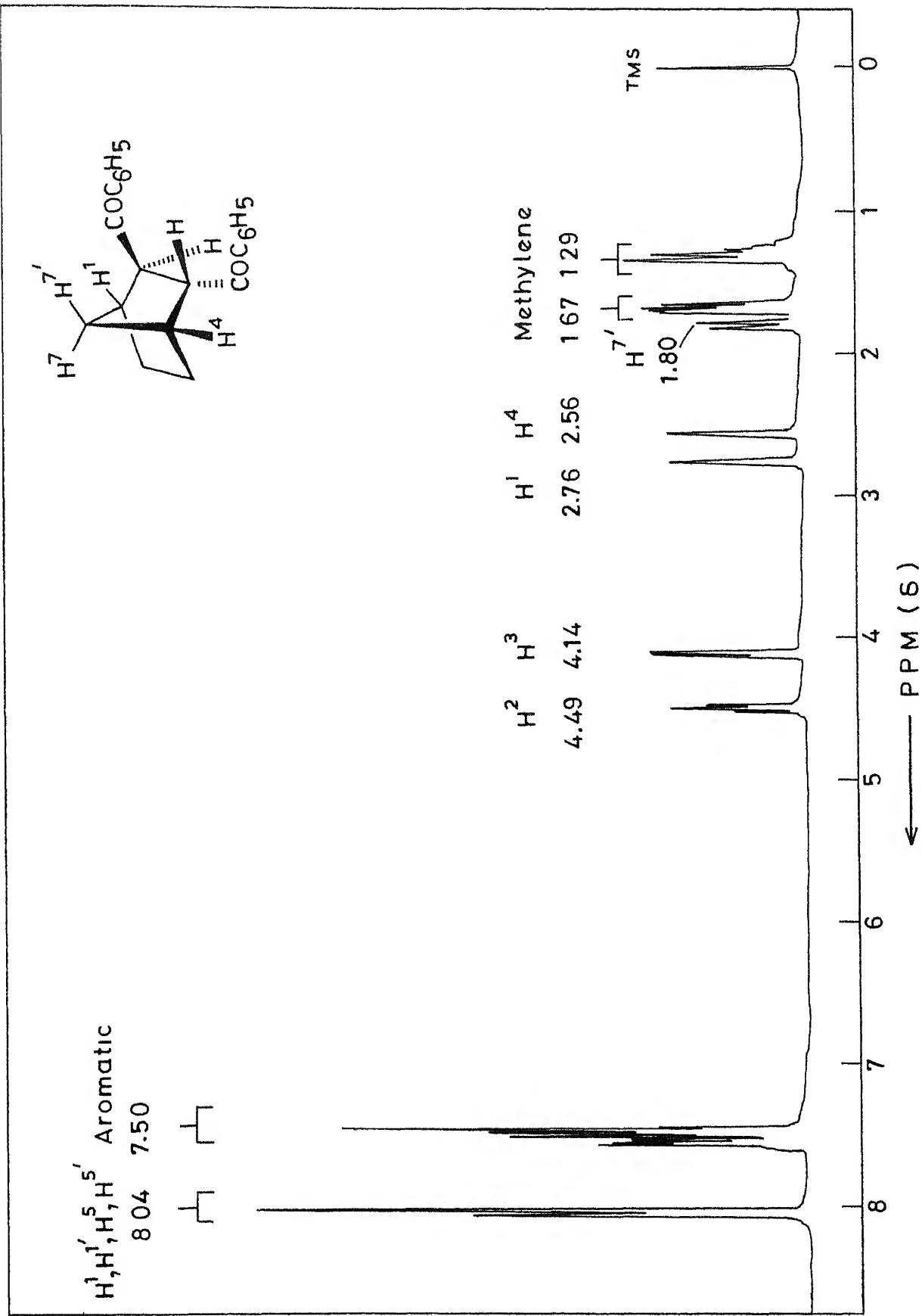


Fig I.12 1H NMR spectrum (270MHz) of 44

observed coupling constant is in tune with reported values for the geminal proton couplings of methylene groups.²² The singlets at δ 2.56 and 2.76 have been assigned to the bridge-head protons H-4 and H-1, respectively, whereas the doublet at δ 4.14 and multiplet at δ 4.49 have been assigned to the endo and exo protons, respectively. The assignment of the high-field multiplet to the exo proton and the low-field multiplet to the endo proton is in accordance with the reported values for similarly positioned protons in a substance such as 2-endo-3-exo-dinitrobicyclo[2.2.1]-heptane.²² The multiplet centred around δ 7.50 was assigned to the ortho protons of the benzoyl groups, whereas the complex multiplet centred around δ 8.04 was assigned to the remaining aromatic protons.

Further support for the structure of 44 was derived from its mass spectrum. The mass spectrum of 44 (Fig. I.13) showed a molecular ion peak at m/e 304 (3). Other prominent peaks in the spectrum were observed at m/e 238 (20), 200 (6), 199 (43), 184 (3), 171 (14), 157 (2), 133 (33), 115 (2), 105 (100), 91 (3), 77 (63), 67 (3), 66 (11) and 55 (9). Some of the probable fragmentation modes of 44 are shown in Scheme I.12.

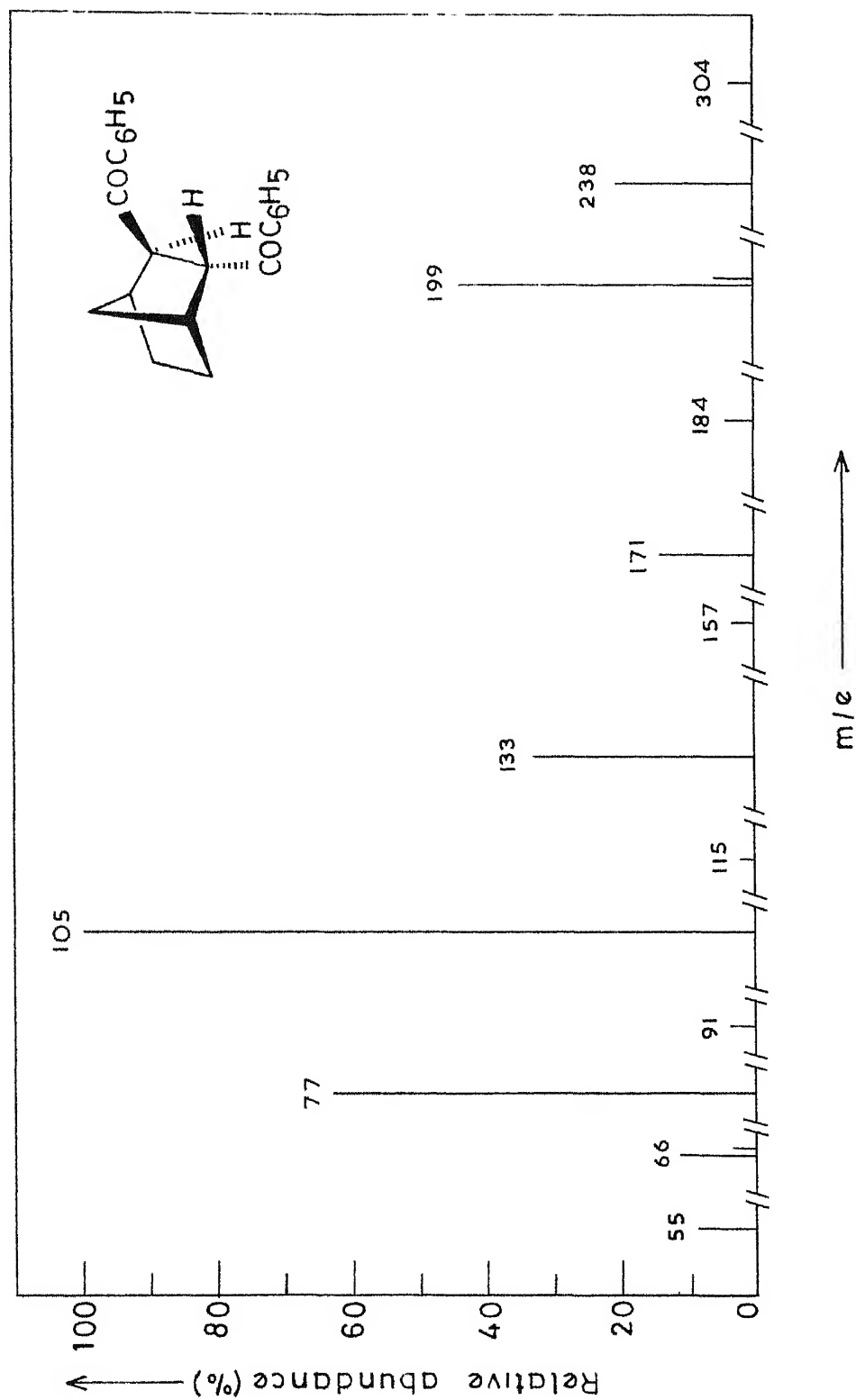
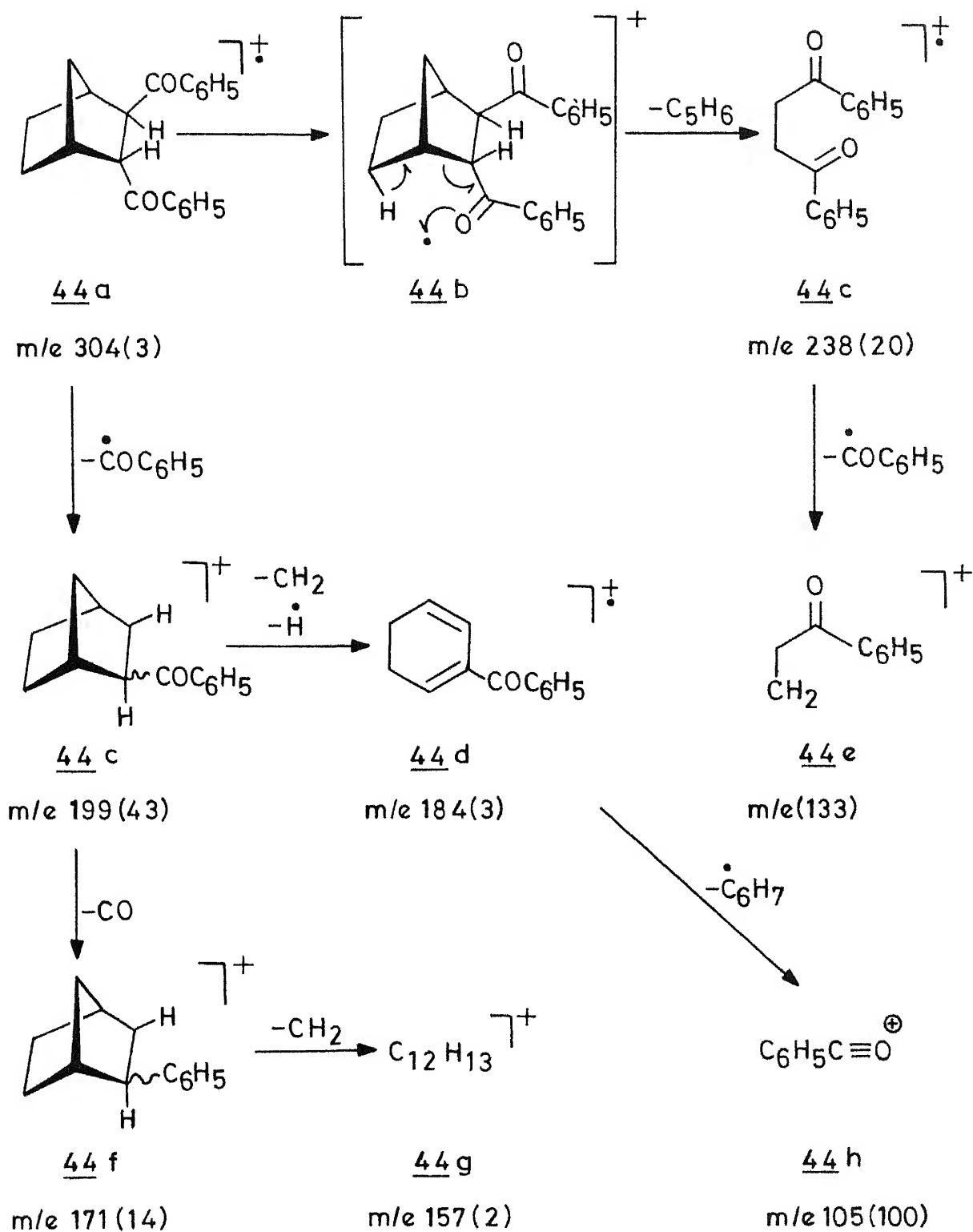


Fig I 13 Mass spectrum of 44.

Scheme I.12



In contrast to the thermal transformation of 25, the thermolysis of 26 gave a 42% yield of a product, identified as 2-benzoyl-3-phenylbicyclo[2.2.2]oct-2-ene (47). The structure of 47 was arrived at on the basis of analytical data and spectral information. Thus, the ^1H NMR spectrum of 47 (Fig. I.14) showed a multiplet centred around δ 1.7 (8 H), due to the methylene protons and a singlet at δ 3.0 (2 H), due to the bridgehead protons. In addition, the spectrum showed two multiplets centred around δ 7.0 (8 H) and 7.5 (2 H). Of these, the multiplet around δ 7.5 was assigned to the ortho protons of benzoyl group, whereas the multiplet around δ 7.0 was assigned to the remaining aromatic protons.

The mass spectrum of 47 (Fig. I.15) showed a molecular ion peak at m/e 288 (84). In addition, the spectrum showed several peaks at m/e 260 (13), 232 (3), 211 (8), 183 (7), 165 (5), 155 (18), 153 (14), 151 (11), 141 (8), 128 (11), 115 (15), 105 (80) and 77 (100). Some of the probable fragmentation modes of 47 are shown in Scheme I.13.

The formation of 44 in the thermolysis of 25 may occur through a disproportionation reaction, perhaps involving radical intermediates. It is interesting to note that none of the expected rearrangement products

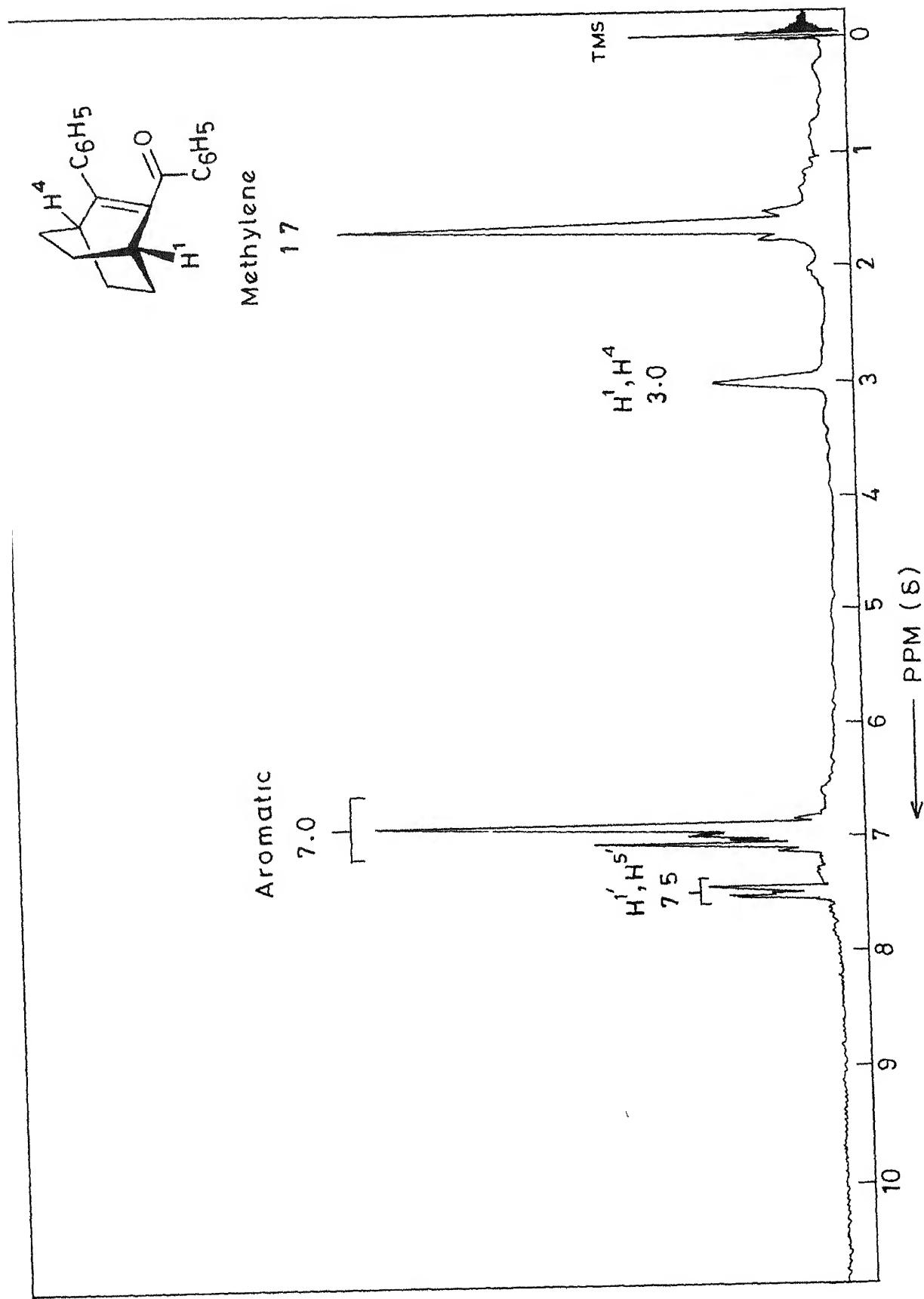


Fig I 14 NMR spectrum (90 MHz) of 47

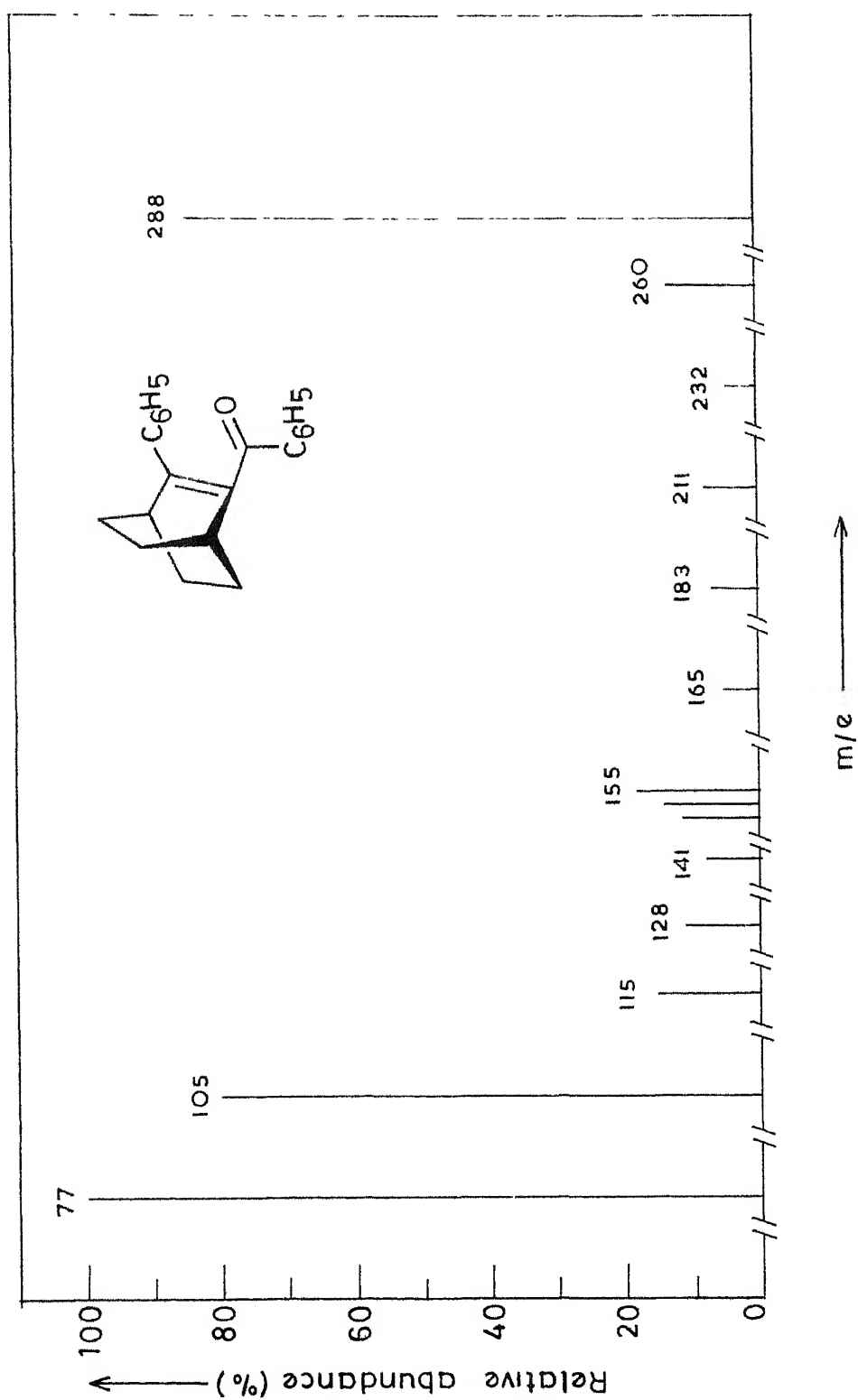
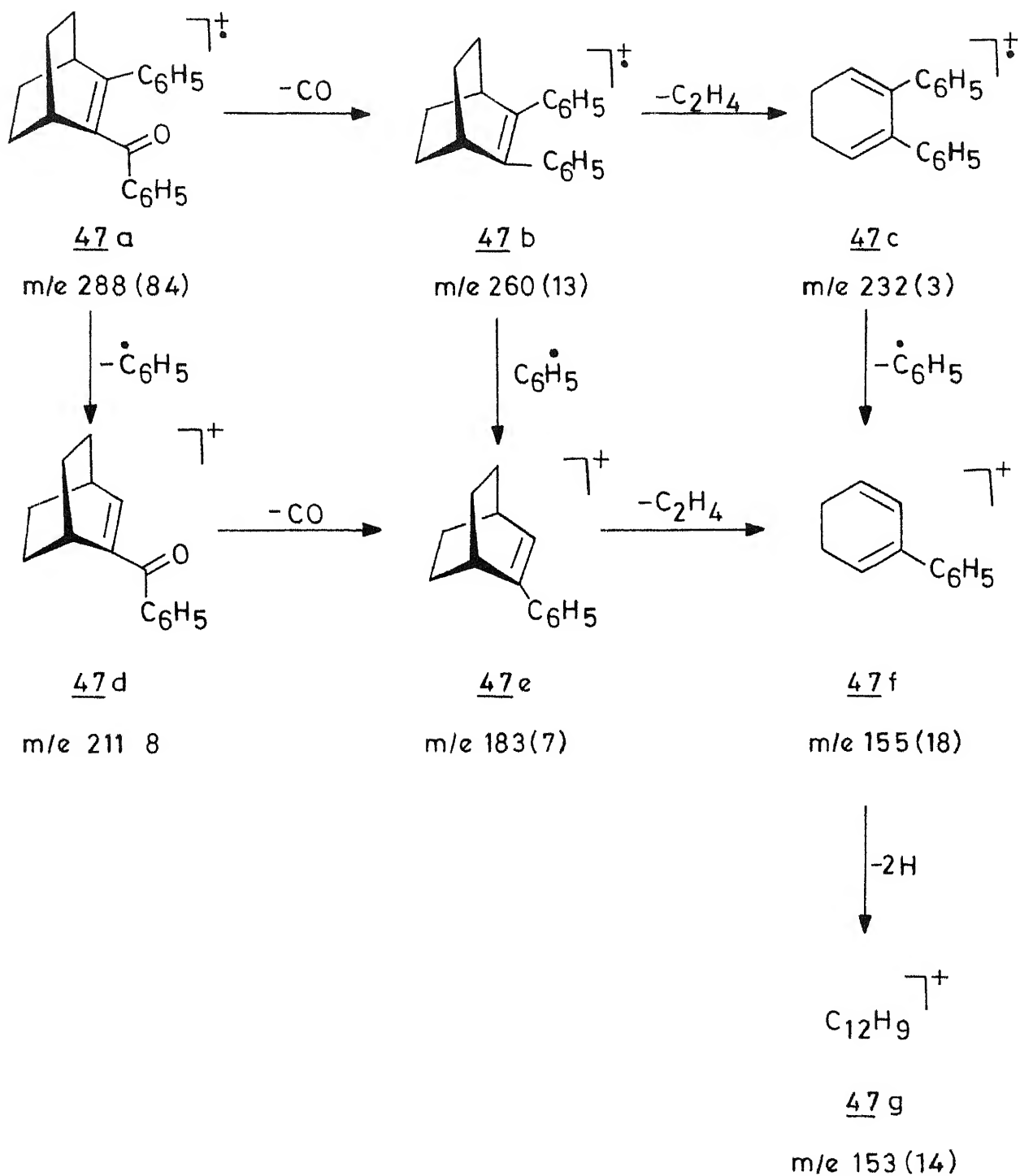


Fig I 15 Mass spectrum of 47.

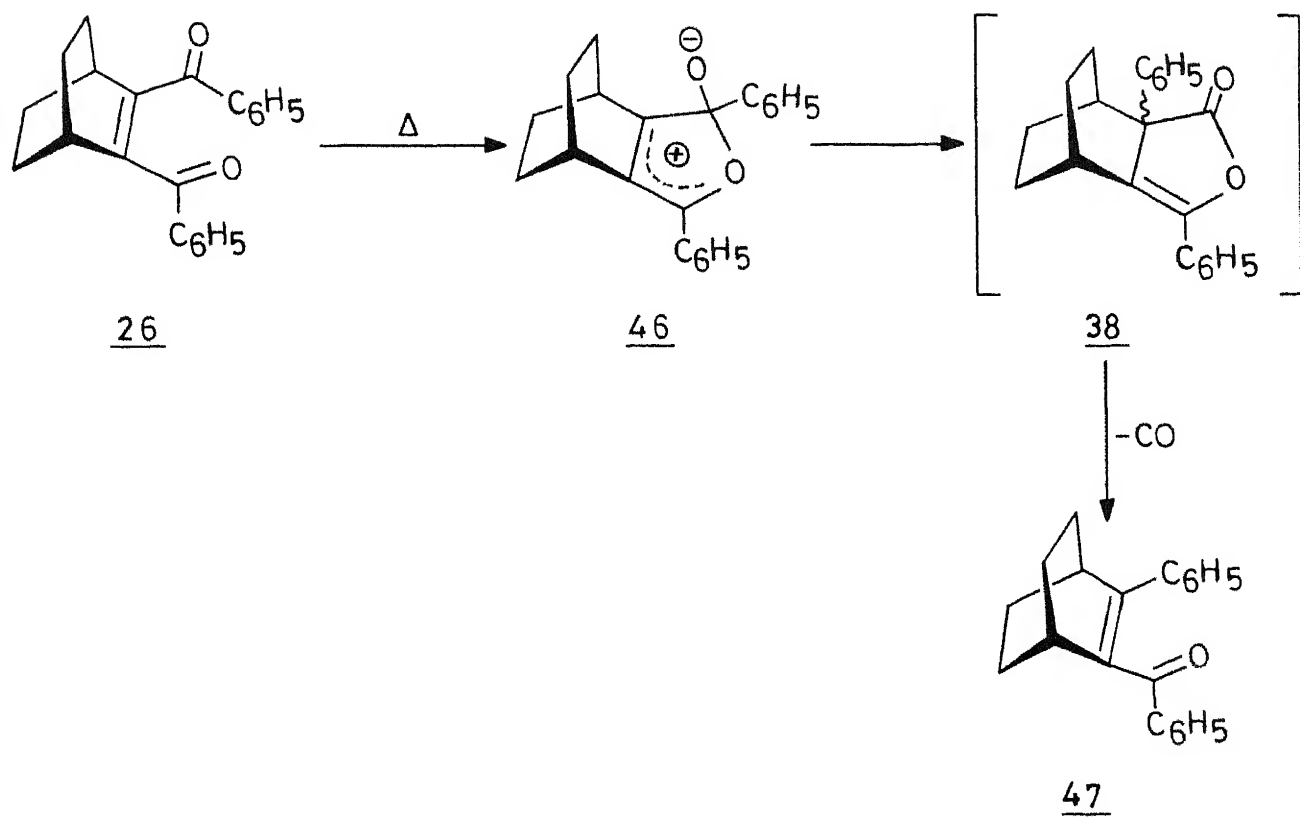
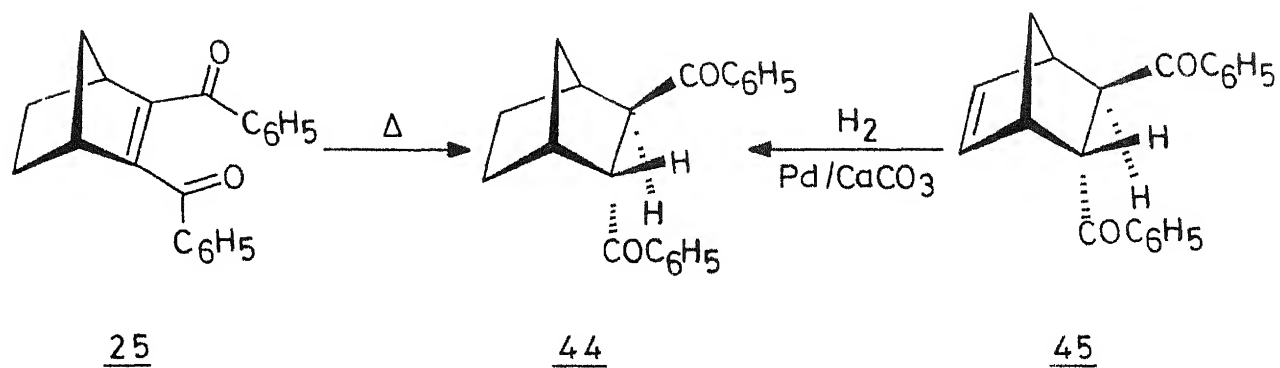
Scheme 1.13



could be isolated from this reaction (Scheme I.14). The formation of 47 in the thermolysis of 26, however, can be rationalized in terms of the initial rearrangement of 26 to the isomeric lactone 38, followed by the loss of CO from 38, under the reaction conditions, as shown in Scheme I.14.

I.4 EXPERIMENTAL

All melting points are uncorrected and were determined on a Mel-Temp melting-point apparatus. The IR spectra were recorded on Perkin-Elmer Model 377 or Model 580 infrared spectrometers. The electronic spectra were recorded either on a Beckman DB spectrophotometer or on a Varian Cary-17D spectrophotometer. The NMR traces were recorded on a Varian A-60 or Brucker WH-270 NMR spectrometer. The mass spectra were recorded on a Varian Mat CH7 mass spectrometer at 70 eV. All the irradiation experiments were carried out either in a Srinivasan-Griffin Rayonet photochemical reactor (3500 Å) or by using a Hanovia 450-W medium-pressure mercury lamp in a quartz-jacketed immersion well. Dry benzene and absolute methanol were used for the photolysis experiments. Petroleum ether used was the fraction, bp 60-80°.

Scheme I 14

I.4.1 Preparation of 2,3-Dibenzoylbicyclo-[2.2.1]hept-2-ene (25)

A solution of 2,3-dibenzoylbicyclo[2.2.1]hepta-2,5-diene (27)^{19,23} (3.0 g, 0.01 mol) was hydrogenated over 5% Pd on CaCO₃ in ethyl acetate for 1/4 hr, at room temperature and 10 psi of hydrogen gas. Removal of the catalyst and evaporation of the solvent under vacuum gave a product, which was recrystallized from ethyl acetate to give 2.8 g (93%) of 25, mp 135° (lit.²³ mp 132.5°).

IR spectrum (KBr) ν_{\max} : 3040, 2970 and 2900 cm⁻¹ ($\nu_{\text{C-H}}$), 1650 cm⁻¹ ($\nu_{\text{C=O}}$) and 1615 cm⁻¹ ($\nu_{\text{C=C}}$).

UV spectrum (methanol) λ_{\max} : 260 nm (ϵ , 14,450).

Mass spectrum m/e (relative intensity): 302 (25), 274 (11), 261 (5), 246 (2), 195 (5), 181 (8), 169 (4), 153 (3), 141 (5), 115 (5), 105 (100), 77 (98), 62 (8) and 51 (5).

I.4.2 Preparation of 2,3-Dibenzoylbicyclo-[2.2.2]oct-2-ene (26)

A solution of 2,3-dibenzoylbicyclo[2.2.2]octa-2,5-diene (28) (3.14 g, 0.01 mol) in ethyl acetate (150 ml) was hydrogenated over 5% Pd on CaCO₃ at room temperature and 10 psi of hydrogen, for 1/2 hr. Removal of the catalyst and evaporation of the solvent under vacuum gave a product, which was recrystallized from ethyl acetate to give 2.8 g (89%) of 26, mp 145°.

Anal. Calcd for $C_{22}H_{20}O_2$: C, 83.03; H, 6.91.

Found: C, 83.71; H, 6.99.

IR spectrum (KBr) ν_{\max} : 3040, 2928 and 2900 cm^{-1} ($\nu_{\text{C-H}}$), 1660 cm^{-1} ($\nu_{\text{C=O}}$), and 1615 cm^{-1} ($\nu_{\text{C=C}}$).

UV spectrum (methanol) λ_{\max} : 260 nm (ϵ , 16,300).

Mass spectrum m/e (relative intensity): 316 (48), 288 (10), 260 (7), 248 (40), 238 (7), 211 (20), 209 (16), 183 (11), 165 (7), 155 (12), 141 (7), 128 (7), 105 (78), 77 (100) and 51 (30).

I.4.3 Photolysis of 2,3-Dibenzoylbicyclo[2.2.1]-hept-2-ene (25) in Benzene

A solution of 25 (1.0 g, 3.3 mmol) in benzene (450 ml) was irradiated for 3 hr, using a Hanovia 450-W medium-pressure mercury lamp, provided with a pyrex filter. The experiment was repeated a few times to photolyse, in all, 3.02 g (10 mmol) of 25. Removal of the solvent under vacuum gave a residual solid, which was chromatographed over silica gel. Elution with a mixture (4:1) of petroleum ether and benzene gave 850 mg (28%) of the unchanged starting material (25), mp 134–135° (mixture melting point).

Subsequent elution of the column with a mixture (1:1) of petroleum ether and benzene gave 480 mg (15%) of 3-(phenoxyphenylmethylene)bicyclo[2.2.1]heptane-2-exo-carboxylic acid (34), mp 190° , after recrystallization from benzene.

Anal. Calcd for $C_{20}H_{20}O_3$: C, 78.75; H, 6.25; Mol. wt., 320. Found: C, 78.91; H, 6.41; Mol. wt., 320 (Mass spectrometry).

IR spectrum (KBr) ν_{\max} : $3550-3250\text{ cm}^{-1}$ (ν_{O-H}), 3140 , 3000 and 2950 cm^{-1} (ν_{C-H}), 1715 cm^{-1} ($\nu_{C=O}$), 1650 , 1600 and 1500 cm^{-1} ($\nu_{C=C}$).

UV spectrum (methanol) λ_{\max} : 229 nm (ϵ , 11,400) and 260 (13,500).

I.4.4 Photolysis of 2,3-Dibenzoylbicyclo[2.2.1]-hept-2-ene (25) in Methanol

A solution of 25 (300 mg, 1 mmol) in methanol (100 ml) was irradiated for 8 hr in a Srinivasan-Griffin Rayonet photochemical reactor, equipped with a 3500 Å light source. The photolysis was repeated several times to photolyse, in all, 1.5 g (5 mmol) of 25. The solvent was removed under vacuum and the residue was chromatographed over silica gel. Elution of the column with a mixture (9:1) of petroleum ether and benzene gave 680 mg

(41%) of methyl 3-(phenoxyphenylmethylene)bicyclo[2.2.1]-heptane-2-exo-carboxylate (33), mp 100°, after recrystallization from benzene.

Anal. Calcd for $C_{22}H_{22}O_3$: C, 79.42; H, 6.58; Mol. wt., 334. Found: C, 79.25; H, 6.35; Mol. wt., 334 (Mass spectrometry).

IR spectrum (KBr) ν_{\max} : 3040, 2980 and 2950 cm^{-1} ($\nu_{\text{C-H}}$), 1720 cm^{-1} ($\nu_{\text{C=O}}$), 1605 and 1502 cm^{-1} ($\nu_{\text{C=C}}$).

UV spectrum (methanol) λ_{\max} : 233 nm (ϵ , 12,600), 260 (19,300) and 274 (9,100).

Further elution of the column with a mixture (4:1) of petroleum ether and benzene gave 170 mg (11%) of the unchanged starting material (25), mp 134-135° (mixture melting point).

I.4.5 Photolysis of 2,3-Dibenzoylbicyclo[2.2.2]-oct-2-ene (26) in Benzene

A solution of 26 (1.1 g, 3.5 mmol) in benzene (500 ml) was irradiated for 3 hr in a Hanovia 450-W medium-pressure mercury lamp, provided with a pyrex filter. The photolysis was repeated with an additional quantity (1.1 g, 3.5 mmol) of 26 and the combined photolysates were worked up by removal of the solvent under vacuum and chromatographing the residual solid thus

obtained, over silica gel. Elution of the column with a mixture (5:1) of petroleum ether and benzene gave 440 mg (20%) of a product, mp 206° , after recrystallization from a mixture (1:1) of petroleum ether and benzene and identified as the lactone 38.

Anal. Calcd for $C_{22}H_{20}O_2$: C, 83.52; H, 6.37; Mol. wt., 316. Found: C, 82.72; H, 6.69; Mol. wt., 316 (Mass spectrometry).

IR spectrum (KBr) ν_{\max} : 3000, 2950 and 2898 cm^{-1} (ν_{C-H}), 1750 cm^{-1} ($\nu_{C=O}$), 1668 and 1660 cm^{-1} ($\nu_{C=C}$).

UV spectrum (methanol) λ_{\max} : 236 nm (ϵ , 21,300), 242 (10,000, sh), 280 (7,100) and 290 (6,500).

Subsequent elution of the column with a mixture (1:1) of petroleum ether and benzene gave 160 mg (7%) of 3-(phenoxyphenylmethylene)bicyclo[2.2.2]octane-2-carboxylic acid (40), mp 218° , after recrystallization from benzene.

Anal. Calcd for $C_{22}H_{22}O_3$: C, 79.05; H, 6.58; Mol. wt., 334. Found: C, 78.42; H, 6.12; Mol. wt., 334 (Mass spectrometry).

IR spectrum (KBr) ν_{\max} : 3550-3250 cm^{-1} (ν_{O-H}), 2980 and 2900 cm^{-1} (ν_{C-H}), 1715 cm^{-1} ($\nu_{C=O}$) and 1660 cm^{-1} ($\nu_{C=C}$).

UV spectrum (methanol) λ_{\max} : 222 nm (ϵ , 12,000) and 260 (12,200).

I.4.6 Photolysis of 2,3-Dibenzoylbicyclo[2.2.2]-oct-2-ene (26) in Methanol

A solution of 26 (316 mg, 1 mmol) in methanol (100 ml) was irradiated for 8 hr in a Srinivasan-Griffin Rayonet photochemical reactor using a 3500 Å light source. The experiment was repeated several times to photolyse, in all, 1.58 g (5 mmol) of 26. Removal of the solvent under vacuum gave a solid residue, which was chromatographed over silica gel. Elution with a mixture (9:1) of petroleum ether and benzene gave 350 mg (20%) of methyl 3-(phenoxy-phenylmethylene)bicyclo[2.2.2]octane-2-carboxylate (39), mp 144°, after recrystallization from a mixture (1:3) of benzene and petroleum ether.

Anal. Calcd for $C_{23}H_{24}O_3$: C, 79.28; H, 6.94; Mol. wt., 348. Found: C, 78.50; H, 6.76; Mol. wt., 348 (Mass spectrometry).

IR spectrum (KBr) ν_{\max} : 3000, 2990 and 2981 cm^{-1} ($\nu_{\text{C-H}}$), 1780 cm^{-1} ($\nu_{\text{C=O}}$), 1630 and 1590 cm^{-1} ($\nu_{\text{C=C}}$).

UV spectrum (methanol) λ_{\max} : 260 nm (ϵ , 19,000) and 275 (9,000).

Further elution of the column with a mixture (2:1) of petroleum ether and benzene gave 0.78 g (49%) of the unchanged starting material (26), mp 144-145° (mixture melting point).

In a repeat run, 1.58 g (5 mmol) of 26 was irradiated in methanol, in several lots, using a Hanovia 450-W medium-pressure mercury lamp, provided with a pyrex filter. Removal of the solvent under vacuum gave a residue, which was chromatographed over silica gel. Elution of the column with a mixture (4:1) of petroleum ether and benzene gave 73 mg (5%) of the lactone 38, mp 206° (mixture melting point).

Further elution of the column with different solvents gave a complex mixture of products, from which no definite product could be isolated.

I.4.7 Base-Catalysed Hydrolysis of Methyl 3-(Phenoxyphenylmethylene)bicyclo[2.2.2]octane-2-carboxylate (39)

A mixture of 39 (100 mg, 0.3 mmol) and 10% aqueous sodium hydroxide (5 ml) was heated around 90-100° for 6 hr. The reaction mixture, on cooling, was acidified with dilute hydrochloric acid to give a solid, which was filtered, washed with water and recrystallized from benzene to give 60 mg (63%) of 3-(phenoxyphenylmethylene)bicyclo[2.2.2]octane-2-carboxylic acid (40), mp 218° (mixture melting point).

I.4.8 Thermolysis of 2,3-Dibenzoylbicyclo[2.2.1]-hept-2-ene (25)

A sample of 25 (600 mg, 2 mmol) was heated around 310° for 1 hr and the reaction mixture was chromatographed over silica gel. Elution with a mixture (4:1) of petroleum ether and benzene gave 160 mg (30%) of 2-endo-3-exo-dibenzoylbicyclo[2.2.1]heptane (44), mp 106° .

Anal. Calcd for $C_{21}H_{20}O_2$: C, 82.88; H, 6.57; Mol. wt., 304. Found: C, 82.94; H, 6.47; Mol. wt., 304 (Mass spectrometry).

IR spectrum (KBr) ν_{\max} : 3080, 2940 and 2870 cm^{-1} (ν_{C-H}), 1665 cm^{-1} ($\nu_{C=O}$), 1595 and 1580 cm^{-1} ($\nu_{C=C}$).

UV spectrum (methanol) λ_{\max} : 210 nm (ϵ , 5,700), 248 (24,500) and 278 (4,150).

I.4.9 Hydrogenation of 2-endo-3-exo-Dibenzoylbicyclo[2.2.1]hept-5-ene (45)

A solution of 45²⁴ (1.56 g, 5 mmol) in acetone (150 ml) was hydrogenated over 5% Pd on calcium carbonate for 1 hr at room temperature and 10 psi of hydrogen gas. After filtering off the catalyst, the solvent was removed under vacuum to give a solid material, which on recrystallization from methanol gave a 1.42 g (93%) of 2-endo-3-exo-dibenzoylbicyclo[2.2.1]heptane (44), mp $105-106^{\circ}$ (mixture melting point).

I.4.10 Thermolysis of 2,3-Dibenzoylbicyclo-
[2.2.2]oct-2-ene (26)

A sample of 26 (1.0 g, 2.3 mmol) was heated, in a sealed tube around 310-320° for 1 hr. The reaction mixture, on cooling, was chromatographed over silica gel. Elution with a mixture (4:1) of petroleum ether and benzene gave 400 mg (44%) of 2-benzoyl-3-phenylbicyclo[2.2.2]oct-2-ene (47), mp 214°, after recrystallization from petroleum ether.

Anal. Calcd for $C_{21}H_{20}O$: C, 87.50; H, 6.90; Mol. wt., 288. Found: C, 87.32; H, 6.60; Mol. wt., 288 (Mass spectrometry).

IR spectrum (KBr) ν_{\max} : 3040 and 2900 cm^{-1} ($\nu_{\text{C-H}}$), 1641 cm^{-1} ($\nu_{\text{C=O}}$), 1620 and 1600 cm^{-1} ($\nu_{\text{C=C}}$).

UV spectrum (methanol) λ_{\max} : 230 nm (ϵ , 8,050), 247 (12,900), 254 (11,200) and 282 (4,700).

I.5 REFERENCES

1. G. W. Griffin and E. J. O'Connell, J. Am. Chem. Soc., 84, 4148 (1962).
2. H. E. Zimmerman, H. G. C. Dürr, R. G. Lewis and S. Bram, J. Am. Chem. Soc., 84, 4149 (1962).
3. A. Padwa, D. Crumrine and A. Shubber, J. Am. Chem. Soc., 88, 3064 (1966).
4. N. Sugiyama and C. Kashima, Bull. Chem. Soc. Jpn., 43, 1875 (1970).
5. H. E. Zimmerman, H. G. C. Dürr, R. S. Givens and R. G. Lewis, J. Am. Chem. Soc., 89, 1863 (1967).
6. S. Lahiri, Ph.D. Thesis, Indian Institute of Technology, Kanpur, 1977.
7. S. Lahiri, V. Dabral, S. M. S. Chauhan, E. Chakachery, C. Vijaya Kumar, J. C. Scaiano and M. V. George, J. Org. Chem., 45, 3782 (1980).
8. M. C. Hamming, "Interpretation of Mass Spectra of Organic Compounds", Academic Press, New York, 1972, p.622.
9. H. Schmid, M. Hochweber and H. van Halban, Helv. Chim. Acta., 30, 1135 (1947).
10. S. Lahiri, V. Dabral and M. V. George, Tetrahedron, 34, 2305 (1979).
11. The laser flash-photolysis studies were carried out by Dr. Juan C. Scaiano at the Radiation Laboratory of the University of Notre Dame (USA), using a Molelectron UV-400 nitrogen laser for excitation.
12. R. D. Small, Jr. and J. C. Scaiano, J. Am. Chem. Soc., 100, 4512 (1978).
13. R. A. Caldwell and D. Creed, J. Am. Chem. Soc., 99, 8360 (1977).

14. M. V. Encinas and J. C. Scalano, J. Photochem., 11, 241 (1979).
15. N. Zinin, Chem. Ber., 5, 1104 (1872).
16. F. R. Japp and F. Klingemann, J. Chem. Soc., 662 (1890).
17. A. H. Blatt, J. Org. Chem., 15, 869 (1950).
18. S. Lahiri, V. Dabral and M. V. George, Tetrahedron Lett., 2259 (1976).
19. S. Lahiri, V. Dabral, M. P. Mahajan and M. V. George, Tetrahedron, 33, 3247 (1977).
20. S. Lahiri, V. Dabral, V. Bhat, E. D. Jemmis and M. V. George, Proc. Indian Acad. Sci., Sect. A, 86A, 1 (1977).
21. D. M. Chipman, S. M. S. Chauhan and M. V. George, J. Org. Chem., 45, 3187 (1980).
22. F. A. Bovey, "NMR Data Tables for Organic Compounds", Volume 1, Interscience Publishers, New York, 1967, p.178.
23. G. Dupont and J. Germain, C. R. Hebd. Seances Acad. Sci., 223, 743 (1946); Chem. Abstr., 41, 2420 (1947).
24. R. Adams and M. H. Gold, J. Am. Chem. Soc., 62, 56 (1940).

CHAPTER II

PHOTOCHEMICAL AND THERMAL TRANSFORMATIONS OF SOME DIBENZOBARRELENE DERIVATIVES

II.1 ABSTRACT

The photochemical and thermal transformations of a few dibenzobarrelene derivatives such as 11,12-dibenzoyl-9,10-dihydro-9,10-ethenoanthracene (34), 11,12-dibenzoyl-9,10-dihydro-9-methyl-9,10-ethenoanthracene (35), 11,12-dibenzoyl-9,10-dihydro-9-hydroxy-9,10-ethenoanthracene (36) and 11,12-dibenzoyl-9,10-dihydro-9,10-dimethyl-9,10-ethenoanthracene (37), have been examined in the present studies. These dibenzobarrelenes 34-37 themselves were prepared through the aluminum chloride catalyzed Diels-Alder reaction of the corresponding anthracenes with dibenzoylacetylene.

Irradiation of 34 in methanol, for example, gave a 52% yield of 1,2-dibenzoyldibenzotricyclo[3.3.0.0^{2,8}]octa-3,6-diene (42) and a small amount (4%) of benzoic acid. There was an increase in the yield of benzoic acid when the irradiation of 34 was carried out in methanol, saturated with oxygen. Irradiation of 34 in acetone, however, gave a 89% yield of 42. Catalytic hydrogenation of 42 over palladium on charcoal gave a 60% yield of 9a,10-dibenzoyl-4b,9,9a,10-tetrahydro-cis-indeno[1,2-a]indene (41), indicating, thereby, that the cyclopropane ring in 42 is cleaved under these conditions.

The irradiation of 35 in benzene gave a 54% yield of 8c,8d-dibenzoyl-4b,8b,8c,8d-tetrahydro-4b-methyldibenzo[a,b]-cyclopropa[c,d]pentalene (47) and a small amount (12%) of benzoic acid. Similar results have been obtained in the irradiation of 35 in solvents such as methanol and acetone. Catalytic hydrogenation of 47 over palladium on charcoal gave 9a,10-dibenzoyl-4b,9,9a,10-tetrahydro-4b-methyl-cis-indeno[1,2-a]indene (50). The irradiation of the hydroxybarrelene derivative 36, in benzene, on the other hand, gave a mixture of 9a,10-dibenzoyl-4b,9,9a,10-tetrahydro-9-oxo-cis-indeno[1,2-a]indene (55) and benzoic acid (4%). Similar results have been obtained when the irradiation of 36 was carried out in acetone.

In contrast to the photoreactions of 34, 35 and 36, the irradiation of 37 gives rise to a mixture of products, depending on the reaction conditions. The irradiation of 37 in benzene, for example, gave a mixture of 2,3-dibenzoyl-2,3-dihydro-1,4-dimethyl-2-benzonaphthalene (60, 12%), 1,4-dibenzoyl-5,8-dimethyl-2,6-dibenzocyclooctatetraene (57, 20%), an isomeric hydroxy compound 63 (45%) and benzoic acid (7%). Similarly, irradiation of 37 in methanol gave a mixture of 60 (25%), 57 (27%) and benzoic acid (8%). On the other hand, the irradiation of 37 in acetone gave a mixture of 9a,10-dibenzoyl-4b,9,9a,10-tetrahydro-4b-methyl-9-methylene-cis-indeno[1,2-a]indene (65, 80%) and benzoic acid (7%).

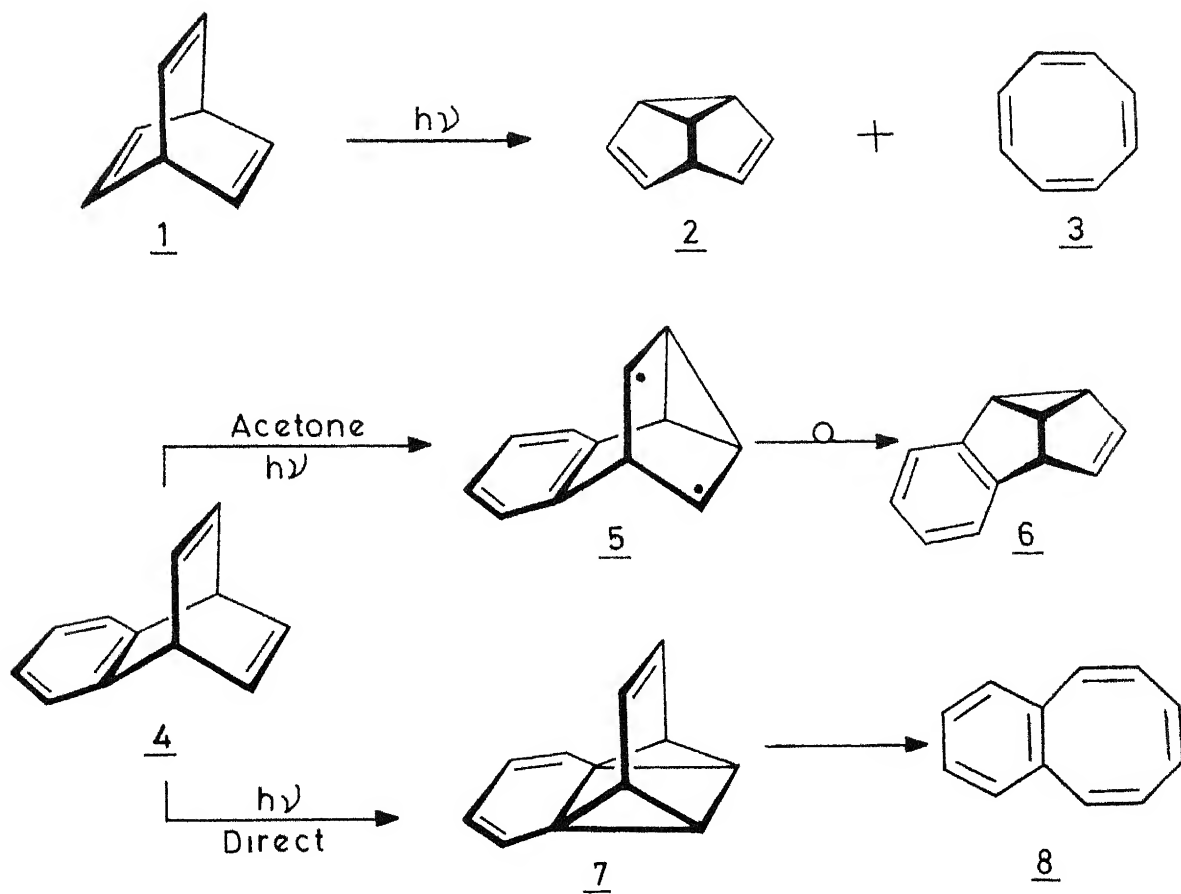
In contrast to the phototransformations of the dibenzobarrelene derivatives 34, 35, 36 and 37, their thermal transformations appear to proceed through a retro-Diels-Alder fragmentation mode. Thus, the thermolysis of 35 around 250° (refluxing diphenyl ether) resulted in the isolation of a 23% yield of 9-methylanthracene, besides polymeric materials and a 27% recovery of the unchanged starting material. Similarly, the thermolysis of 37 around 300° gave a 16% yield of 9,10-dimethylanthracene, along with a small amount of benzoic acid (6%). In contrast, the thermolysis of 36 in refluxing diphenyl ether gave a 26% yield of anthraquinone, besides polymeric materials.

Reasonable mechanisms have been suggested for the formation of the different products in the photochemical and thermal transformations of the dibenzobarrelenes 34, 35, 36 and 37.

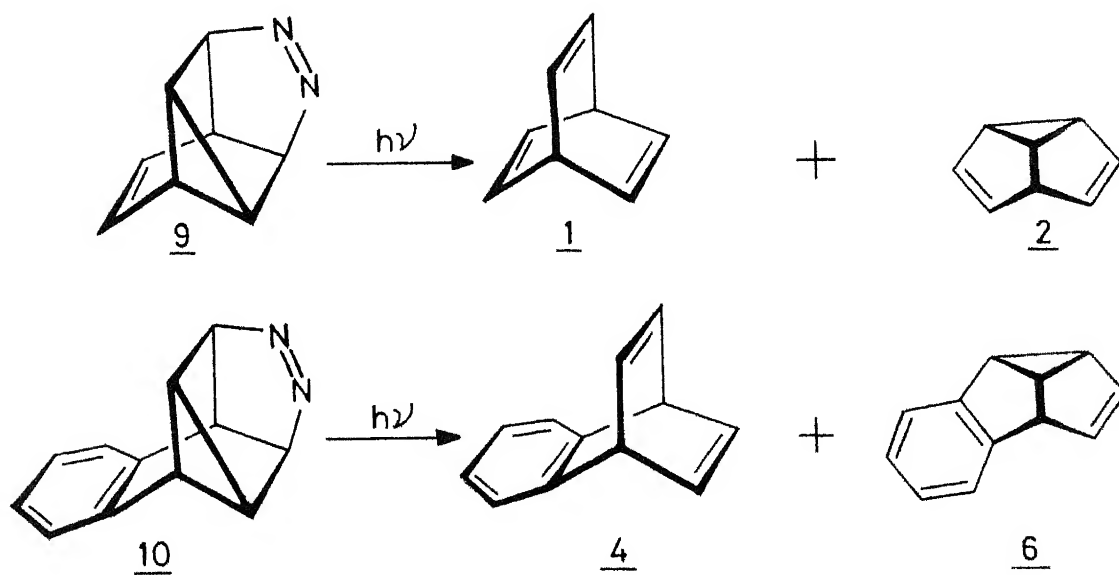
II.2 INTRODUCTION

Zimmerman and coworkers¹ had reported that barrelene (1) undergoes a facile photoisomerization of the di- π -methane type to give the semibullvalene (2). Subsequent studies²⁻⁴ have shown that the direct irradiation of barrelene 1 leads primarily to cyclooctatetraene (3), whereas the semibullvalene (2), is formed in major amounts under sensitized irradiation conditions (Scheme II.1). Similarly, the acetone-sensitized irradiation of the benzobarrelene (4) has been reported^{5,6} to give the benzosemibullvalene 6, whereas the direct irradiation of 4 leads to the benzocyclooctatetraene (8) (Scheme II.1). It has been shown on the basis of deuterium labelling studies that in the case of acetone-sensitized rearrangement of 4, the reaction proceeds through an initial vinyl-vinyl bridging to give the diradical intermediate 5, which subsequently reorganizes to give 6. In the case of direct irradiation, however, an initial benzo-vinyl bridging is involved to give the $[\pi^2s + \pi^2s]$ type of addition product 7, which then is transformed to 8.⁶ Zimmerman and coworkers^{7,8} have actually demonstrated the involvement of diradical intermediates such

Scheme II.1



Scheme II.2



as 5 in the phototransformations of barrelene and benzobarrelene derivatives, through the irradiation of the appropriate substrates which will generate such diradical intermediates, under these conditions. Thus, it has been shown that the sensitized irradiation of the diazo compound 9, gives exclusively the semibullvalene (2, 100%), whereas the direct irradiation leads to a mixture of 2 (73%) and the barrelene (1, 24%), arising through a Gröb-type of fragmentation⁹ of the initially formed singlet diradical (Scheme II.2). Similarly, the sensitized irradiation of the diazo compound 10 gives exclusively 6 (48%), whereas the direct irradiation of 10 gives a mixture of 4 (35%) and 6 (10%) (Scheme II.2).⁷

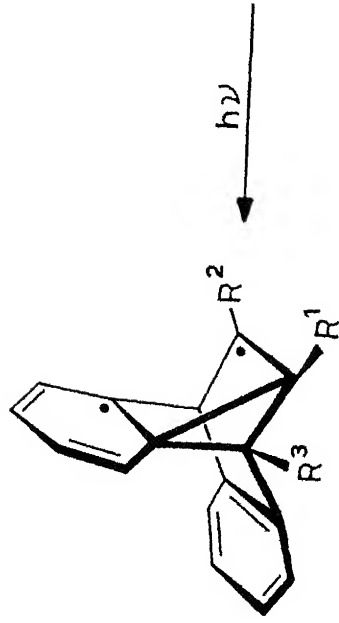
Numerous reports have appeared in the literature on the phototransformations of barrelenes,¹⁰⁻¹⁴ benzobarrelenes,¹⁵⁻²⁷ naphthobarrelenes,²⁸⁻³⁴ dibenzobarrelenes,³⁵⁻⁴⁰ and other barrelene derivatives.⁴¹⁻⁴³ An attempt will be made to highlight briefly some of the salient features of these rearrangements, particularly with respect to the substituent effects and regiospecificity.

It has been generally observed that substituents in the bridgehead and other appropriate positions play a dominant role concerning the regiospecificity⁴⁴ of these rearrangements. Thus, it has been observed that the photorearrangement of the dibenzobarrelene 12a, containing a carbomethoxy group on the vinyl moiety, gives rise to, exclusively the dibenzosemibullvalene derivative 15a (75%), whereas the irradiation of 12b,

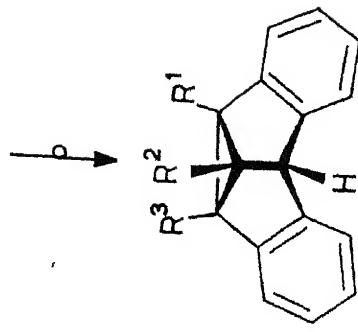
having a carbomethoxy group at the bridgehead position gives a mixture of the dibenzosemibullvalenes, 14 (30%) and 15b (61%), respectively (Scheme II.3).³⁵ It has been suggested that the photorearrangement of 12b, for example, proceeds through the diradical intermediate 13b, which is more stabilized, when compared to 11b. In the case of 12b, however, it appears that the diradical species 11b, containing a cyclopropane ring, bearing an electron withdrawing group is destabilized, when compared to the alternate diradical species 13b. It is interesting to note that the dibenzobarrelene 12c, containing both acetate and the carbomethoxy substituents, on irradiation gives exclusively the dibenzobarrelene derivative 15c (60%), arising through the intermediate 13c (Scheme II.3).³⁸

Apart from electronegativity considerations, the ability of substituents to stabilize the odd electron centres in the diradical intermediates also play a part in the regio-specificity of these rearrangements. It has been observed that the irradiation of the dibenzobarrelenes 16a-g, leads to the dibenzosemibullvalenes 18a-g, in yields ranging between 74-90% and presumably, involving the diradical intermediates 17a-g (Scheme II.4).^{35,39} The photoisomerization of 16e, containing radical stabilizing groups such as carbomethoxy, for example, has been found to yield the corresponding dibenzosemibullvalene 18e, in a nearly quantitative yield (96%), whereas a slight retarding effect of the highly

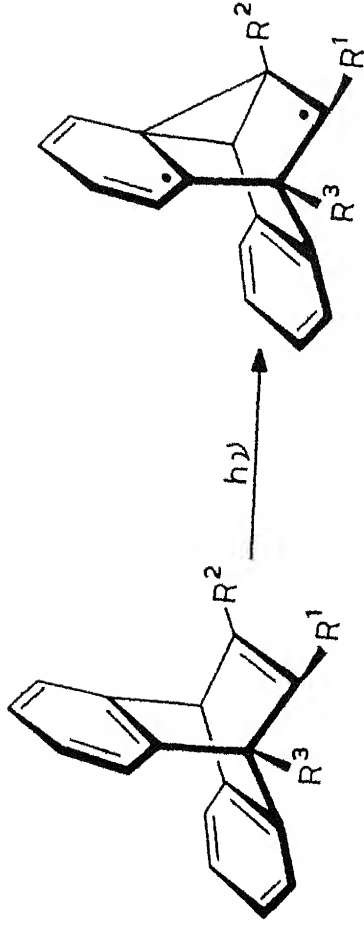
Scheme II 3



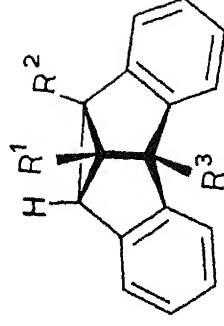
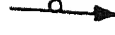
- 11 a) $R^1 = \text{COOCH}_3, R^2 = R^3 = \text{H}$
 b) $R^1 = R^2 = \text{H}, R^3 = \text{COOCH}_3$
 c) $R^1 = R^2 = \text{COOCH}_3, R^3 = \text{OCOCH}_3$



- 14 $R^1 = R^2 = \text{H}, R^3 = \text{COOCH}_3$

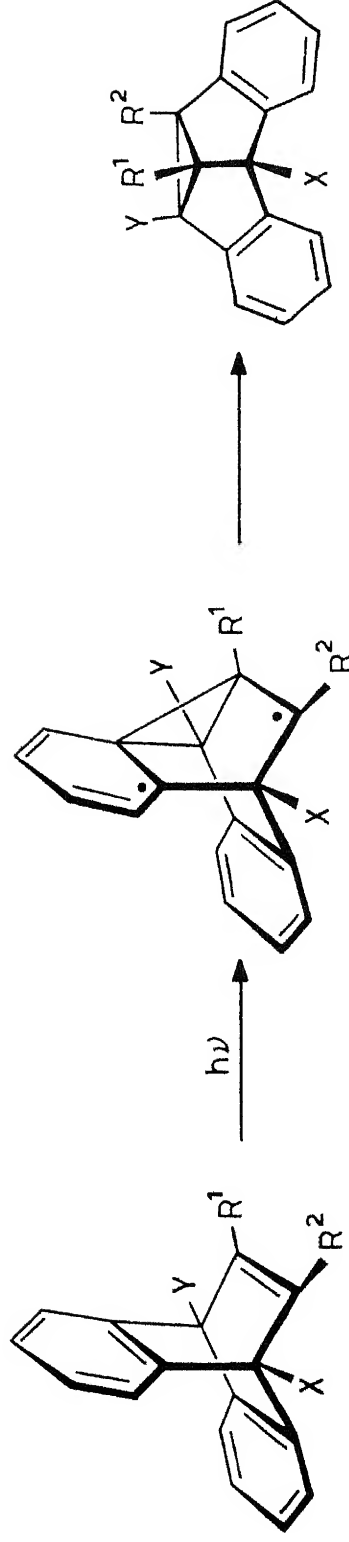


- 12 a) $R^1 = \text{COOCH}_3, R^2 = R^3 = \text{H}$
 b) $R^1 = R^2 = \text{H}, R^3 = \text{COOCH}_3$
 c) $R^1 = R^2 = \text{COOCH}_3, R^3 = \text{OCOCH}_3$



- 15 a) $R^1 = \text{COOCH}_3, R^2 = R^3 = \text{H}$
 b) $R^1 = R^2 = \text{H}, R^3 = \text{COOCH}_3$
 c) $R^1 = R^2 = \text{COOCH}_3, R^3 = \text{OCOCH}_3$

Scheme II 4



- 16 a) $R^1=Y=H, R^2=COOEt, X=OH$
 b) $R^1=Y=H, R^2=COOMe, X=Me$
 c) $R^1=X=H; R^2=COOMe, Y=Me$
 d) $R^1=R^2=X=Y=H$
 e) $R^1=R^2=COOMe, X=Y=H$
 f) $R^1=R^2=CN, X=Y=H$
 g) $R^1=R^2=CF_3, X=Y=H$

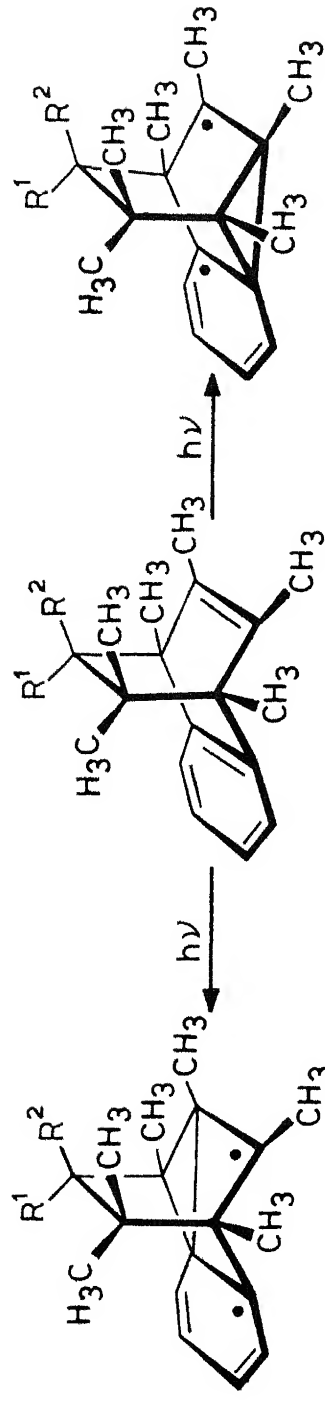
- 17 a) $R^1=Y=H; R^2=COOEt, X=OH$
 b) $R^1=Y=H, R^2=COOMe, X=Me$
 c) $R^1=X=H, R^2=COOMe, Y=Me$
 d) $R^1=R^2=X=Y=H$
 e) $R^1=R^2=COOMe, X=Y=H$
 f) $R^1=R^2=CN, X=Y=H$
 g) $R^1=R^2=CF_3, X=Y=H$

- 18 a) $R^1=COOEt, R^2=Y=H, X=OH$
 b) $R^1=COOMe, R^2=Y=H, X=Me$
 c) $R^1=COOMe, R^2=X=H; Y=Me$
 d) $R^1=R^2=X=Y=H$
 e) $R^1=R^2=COOMe, X=Y=H$
 f) $R^1=R^2=CN, X=Y=H$
 g) $R^1=R^2=CF_3, X=Y=H$

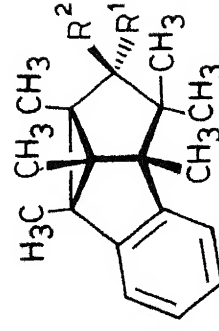
electronegative trifluoromethyl groups, has been observed in the photoisomerization of 16g, leading to 18g (74%).

A somewhat different type of regioselectivity and regioselectivity has been observed by Hart et al.^{36,37} in the case of a few barrelene derivatives, containing, syn and anti positioned hydroxyl and acetate functionalities. Thus, it has been observed that the irradiation of the syn alcohol 20a and the syn acetate 20b gives exclusively the regiospecific isomers, 23a and 23b, respectively (Scheme II.5). In contrast, the irradiation of the anti alcohol 20c gave a mixture of the regioselective isomers 22a (30%) and 23c (45%). Similarly, the irradiation of the anti acetate 20d, gave a mixture of 22b (18%) and 23d (37%). It has been suggested that the oxygen functionality in the proximal diradical 21 renders it more stable than the distal diradical 19 and thereby, accounting for the observed stereospecificity in the phototransformations of 20a and 20b.

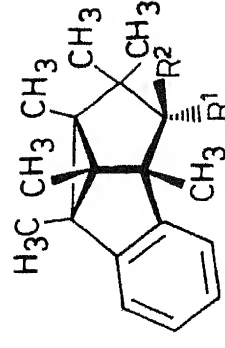
The diradical intermediates involved in the phototransformations of barrelenes have been known to be stabilized by the presence of suitably positioned functional groups. Thus, it has been observed³⁸ that the photoisomerization of the barrelenes 25a and 25b in acetone gives exclusively the keto diester 28 in 70% and 63% yields, respectively and presumably arising through the corresponding dibenzosemibullvalenes 29a and 29b, respectively. None of the isomeric dibenzosemibullvalenes 27a and 27b have been observed in these reactions. It



- 20 a) $R^1 = OH, R^2 = H$
 b) $R^1 = OCOCH_3, R^2 = H$
 c) $R^1 = H, R^2 = OH$
 d) $R^1 = H, R^2 = OCOCH_3$



- 22 a) $R^1 = H, R^2 = OH$
 b) $R^1 = H, R^2 = OCOCH_3$

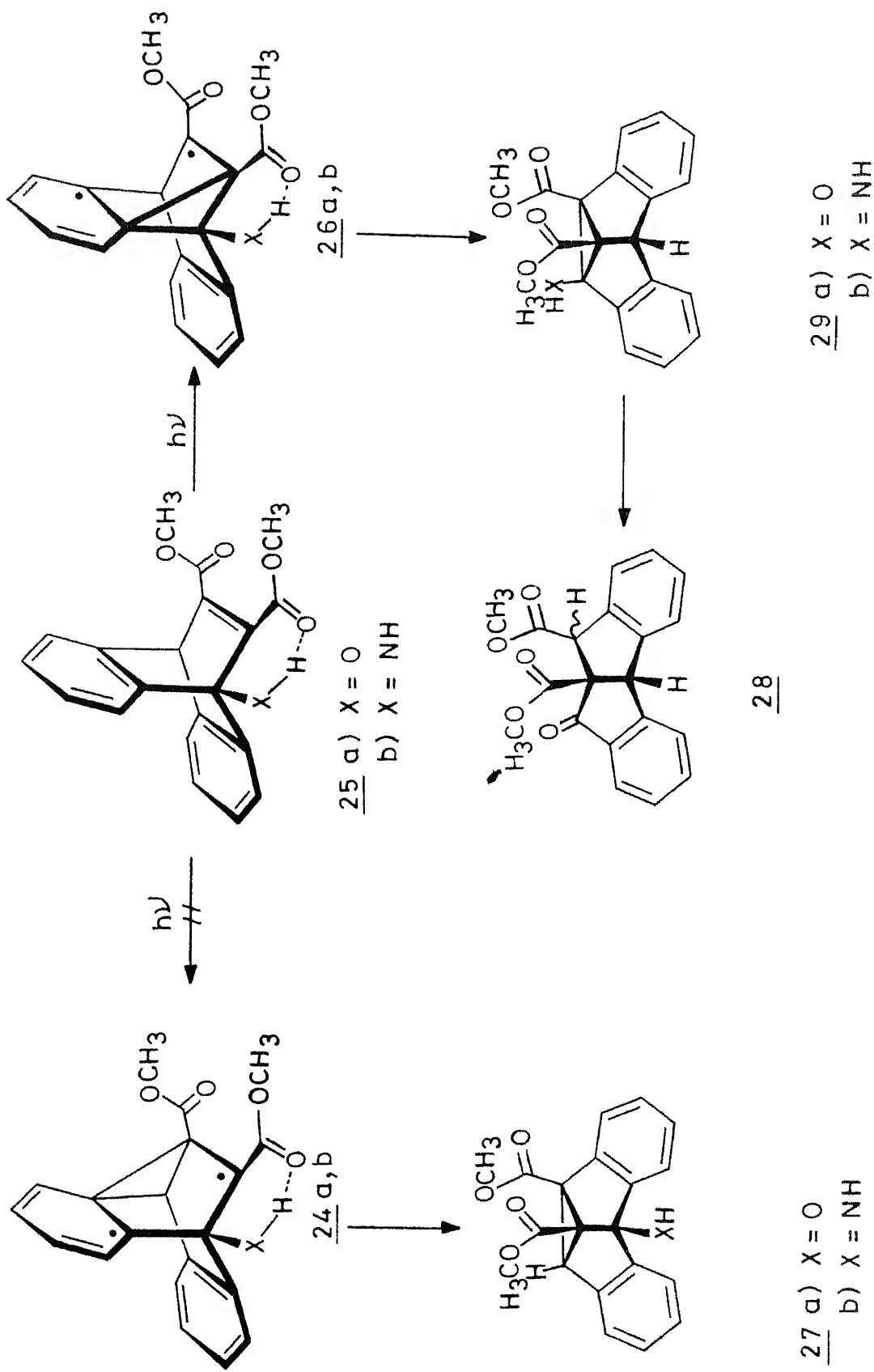


- 23 a) $R^1 = OH, R^2 = H$
 b) $R^1 = OCOCH_3, R^2 = H$
 c) $R^1 = H, R^2 = OH$
 d) $R^1 = H, R^2 = OCOCH_3$

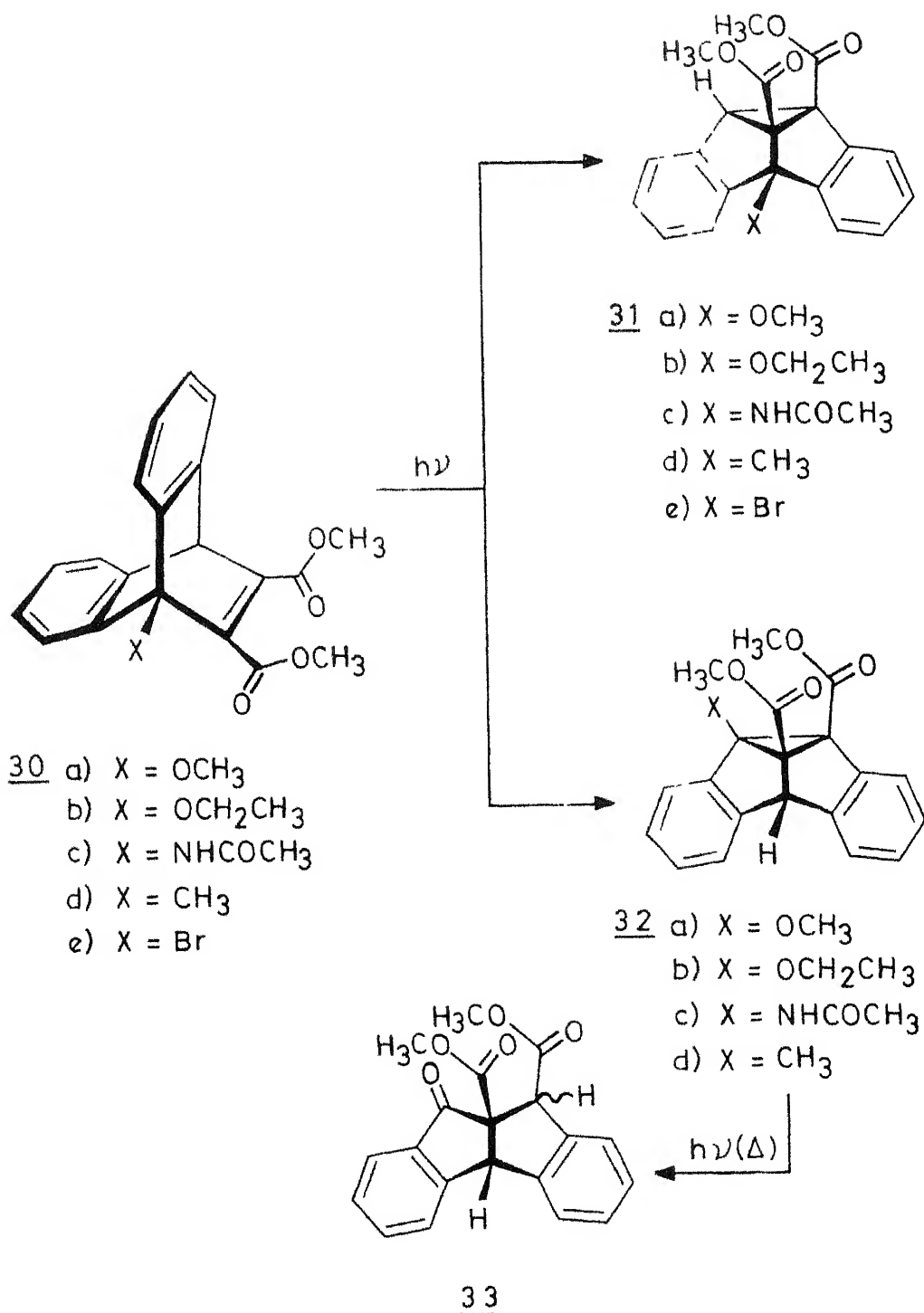
has been suggested that the diradical intermediates 26a and 26b are more stabilized due to hydrogen bonding possibility, when compared to 24a and 24b, involved in the alternative pathway and hence the observed regiospecificity in the photoisomerization of 25a and 25b (Scheme II.6).

Substituents in the bridgehead positions of barrelenes have been shown to influence the regiospecificity in the photoisomerization reactions. In the photoisomerizations of the barrelenes 30a-c, for example, it has been observed that a mixture of the dibenzosemibullvalenes 31a-c and the keto diester 33, arising from the corresponding dibenzosemibullvalenes 32a-c, is formed. Similarly, the photoisomerization of 30d gave a mixture of the dibenzosemibullvalenes, 31d and 32d. In contrast, the irradiation of the bromo derivative 30e gave exclusively the dibenzosemibullvalene 31e (55%) (Scheme II.7).³⁹

The object of the present investigation has been to examine the photoisomerizations of a few dibenzobarrelene derivatives containing cis-1,2-dibenzoylalkene functionalities and also other substituent groups at the bridgehead positions, with a view to examining the nature of the products formed in these transformations and also to study the role of the different substituents in the photoisomerizations of barrelenes. The dibenzobarrelene derivatives that we have examined include, 11,12-dibenzoyl-9,10-dihydro-9,10-ethenoanthracene (34),



Scheme II.7



11,12-dibenzoyl-9,10-dihydro-9-methyl-9,10-ethenoanthracene (35), 11,12-dibenzoyl-9,10-dihydro-9-hydroxy-9,10-ethenoanthracene (36) and 11,12-dibenzoyl-9,10-dihydro-9,10-dimethyl-9,10-ethenoanthracene (37).

II.3 RESULTS AND DISCUSSION

II.3.1 Preparation of 11,12-Dibenzoyl-9,10-dihydro-9,10-ethenoanthracenes

It has been reported that 11,12-dibenzoyl-9,10-dihydro-9,10-ethenoanthracene (34), 11,12-dibenzoyl-9,10-dihydro-9-methyl-9,10-ethenoanthracene (35) and 11,12-dibenzoyl-9,10-dihydro-9,10-dimethyl-9,10-ethenoanthracene (37) are prepared by heating at elevated temperatures, a mixture of the appropriate anthracene with dibenzoylacetylene.⁴⁵ Also, it has been shown that 34 could be conveniently prepared through the aluminum chloride-catalysed reaction between anthracene and dibenzoylacetylene.⁴⁶ In the present studies, we have found that the 11,12-dibenzoyl-9,10-dihydro-9,10-ethenoanthracenes 35, 36 and 37 can be conveniently prepared, in yields ranging between 72-85%, by the treatment of the respective anthracene derivatives with dibenzoylacetylene in presence of anhydrous aluminum chloride. Thus, the reaction of anthranol with DBA in the presence of anhydrous aluminum chloride in methylene chloride at room temperature, for example, gave a 72% yield of 11,12-dibenzoyl-9,10-dihydro-9-hydroxy-9,10-ethenoanthracene

(36). The structure of 36 was established on the basis of analytical data and spectral evidences. The ^1H NMR spectrum of 36 (Fig. II.1), for example, showed a singlet at δ 5.10 (1 H), assigned to the bridgehead proton and a second singlet at δ 5.60 (1 H, D_2O -exchangeable), assigned to the hydroxyl proton. The complex multiplets centred around δ 7.35 (14 H) and 7.75 (4 H) were assigned to the aromatic protons.

Although the preparation of the 11,12-dibenzoyl-9,10-dihydro-9,10-ethenoanthracenes 34, 35 and 37 had been reported earlier, there has been no mention in the literature of their NMR spectra. In the present studies, we have examined the ^1H NMR spectra and the ^{13}C NMR spectra of 34, 35 and 37, primarily with a view to comparing them with those of the corresponding photoproducts.

Earlier, Lahiri⁴⁰ had reported that the ^1H NMR spectrum of 34 shows a singlet at δ 5.66 (2 H), due to the bridgehead protons and a complex multiplet centred around δ 7.25 (14 H), due to the aromatic protons. The ^{13}C NMR spectrum of 34 (Fig. II.2) has been found to show several signals at δ 53.81, 123.77, 125.37, 128.00, 128.39, 132.59, 137.37, 143.90, 153.19 and 194.10. Of these, the signal at δ 53.81 is assigned to the bridgehead carbons, whereas the one at δ 194.10 is assigned to the carbonyl carbons.^{47,48} The ^1H NMR spectrum of 35 (Fig. II.3) showed a singlet at δ 2.09 (3 H) due to the methyl protons, a second singlet at δ 5.64 (1 H), due to the

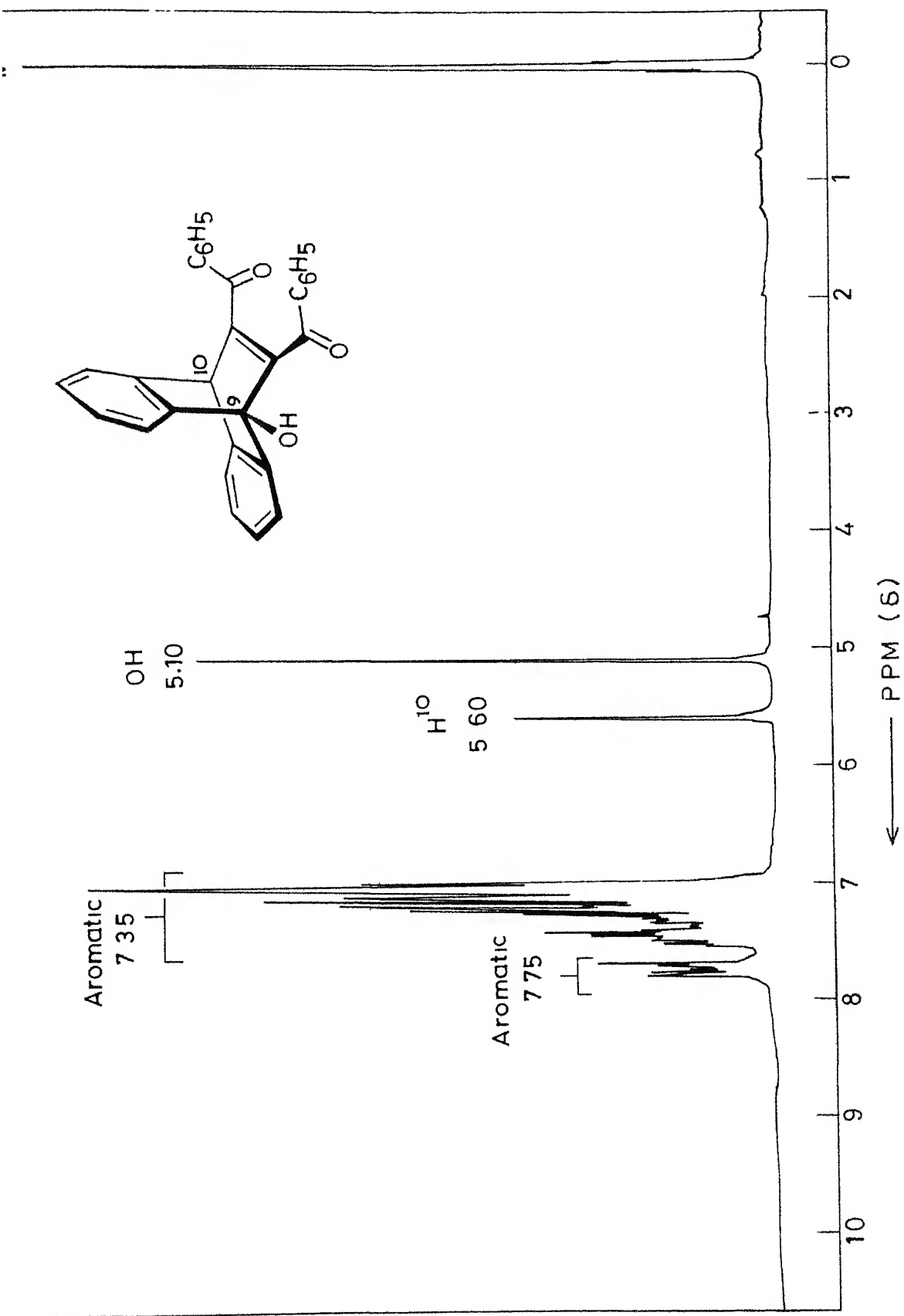


Fig II.1 ^1H NMR spectrum (80 MHz) of 36

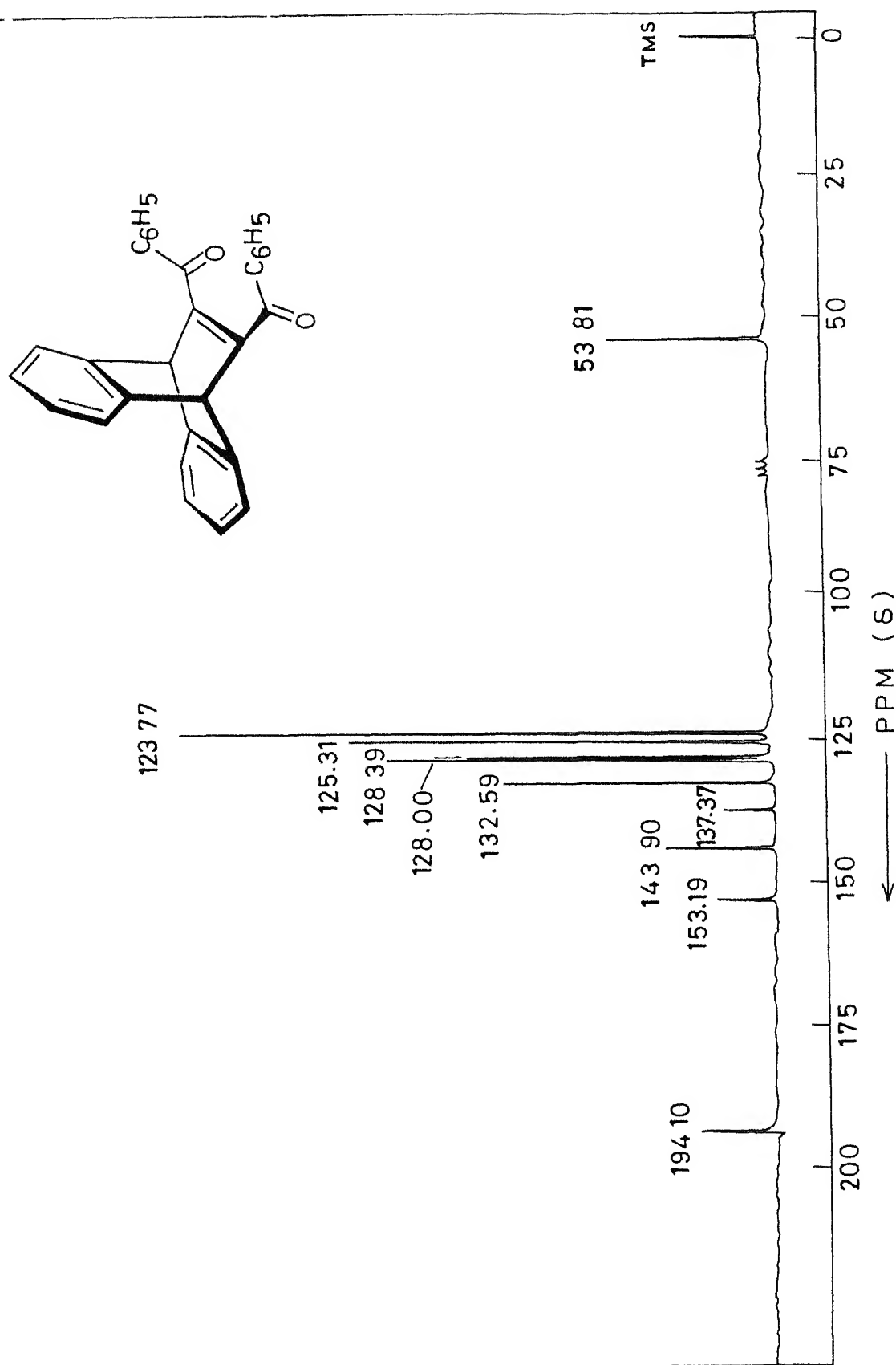


Fig II 2 ¹³C NMR spectrum (25.2 MHz) of 34

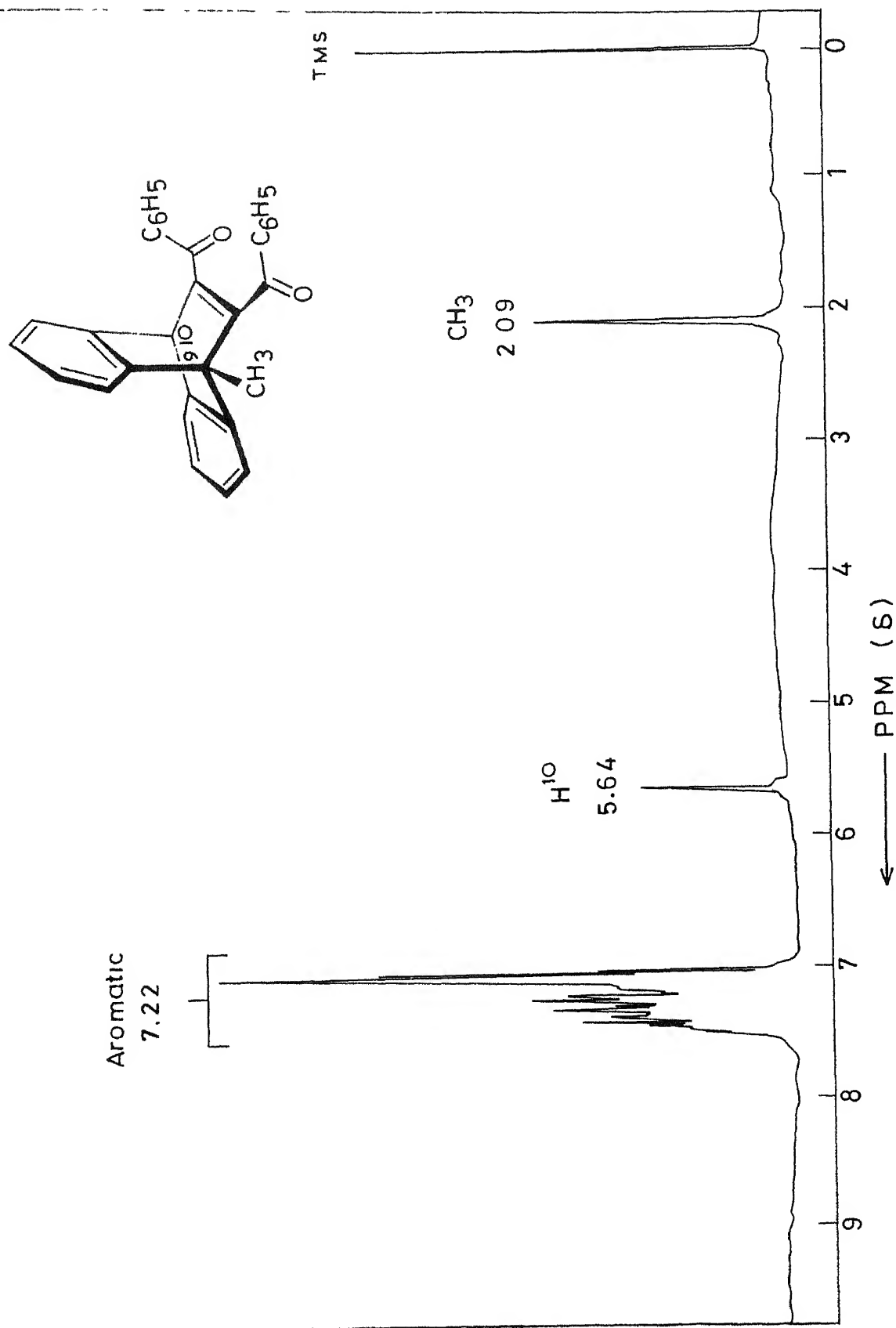


Fig. II.3 ^1H NMR spectrum (100 MHz) of **35**

bridgehead proton and a complex multiplet centred around δ 7.22 (18 H) due to the aromatic protons. The ^{13}C NMR spectrum of 35 (Fig. II.4) showed a signal at δ 13.29 due to the methyl carbon, two signals at δ 52.36 and 52.59, due to the bridgehead carbons and two signals at δ 193.37 and 195.18, due to the carbonyl carbons. In addition, the spectrum showed signals at δ 121.23, 123.46, 125.03, 125.19, 127.88, 128.19, 128.35, 128.89, 132.44, 133.12, 137.19, 145.45, 146.04, 150.59 and 158.23 due to the different sp^2 carbon atoms present in 35. The ^1H NMR spectrum of 37 (Fig. II.5), likewise, showed a singlet at δ 2.11 (6 H) due to the methyl protons and a complex multiplet centred around δ 7.25 (18 H), due to the aromatic protons. The ^{13}C NMR spectrum of 37 (Fig. II.6) showed a signal at δ 13.48 due to the methyl carbons, a second signal at δ 50.68 due to the bridgehead carbons and one at δ 195.36, due to the carbonyl carbons. The remaining sp^2 carbons in 37 showed signals at δ 120.61, 124.73, 128.11, 129.33, 133.36, 136.95, 147.56 and 153.65.

II.3.2 Phototransformations of 11,12-Dibenzoyl-9,10-dihydro-9,10-ethenoanthracenes

It has been shown earlier⁴⁹ that the phototransformations of cis-1,2-dibenzoylalkenes lead to a variety of products, arising through the initial excitation of the dicarbonylalkene chromophore. In the case of 11,12-dibenzoyl-9,10-dihydro-9,10-ethenoanthracenes such as 34, 35, 36

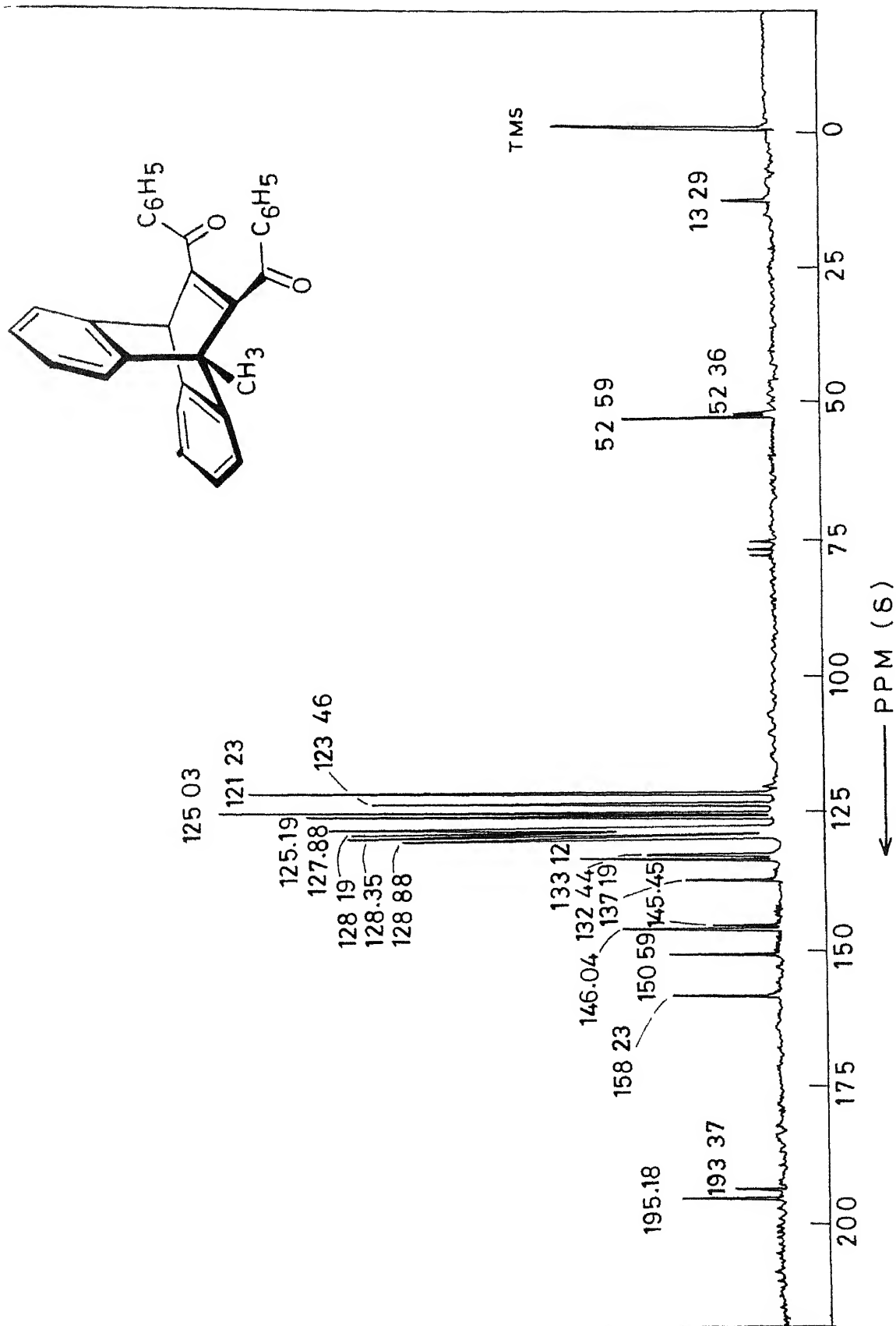


Fig. II 4 ¹³C NMR spectrum (25.2 MHz) of **35**

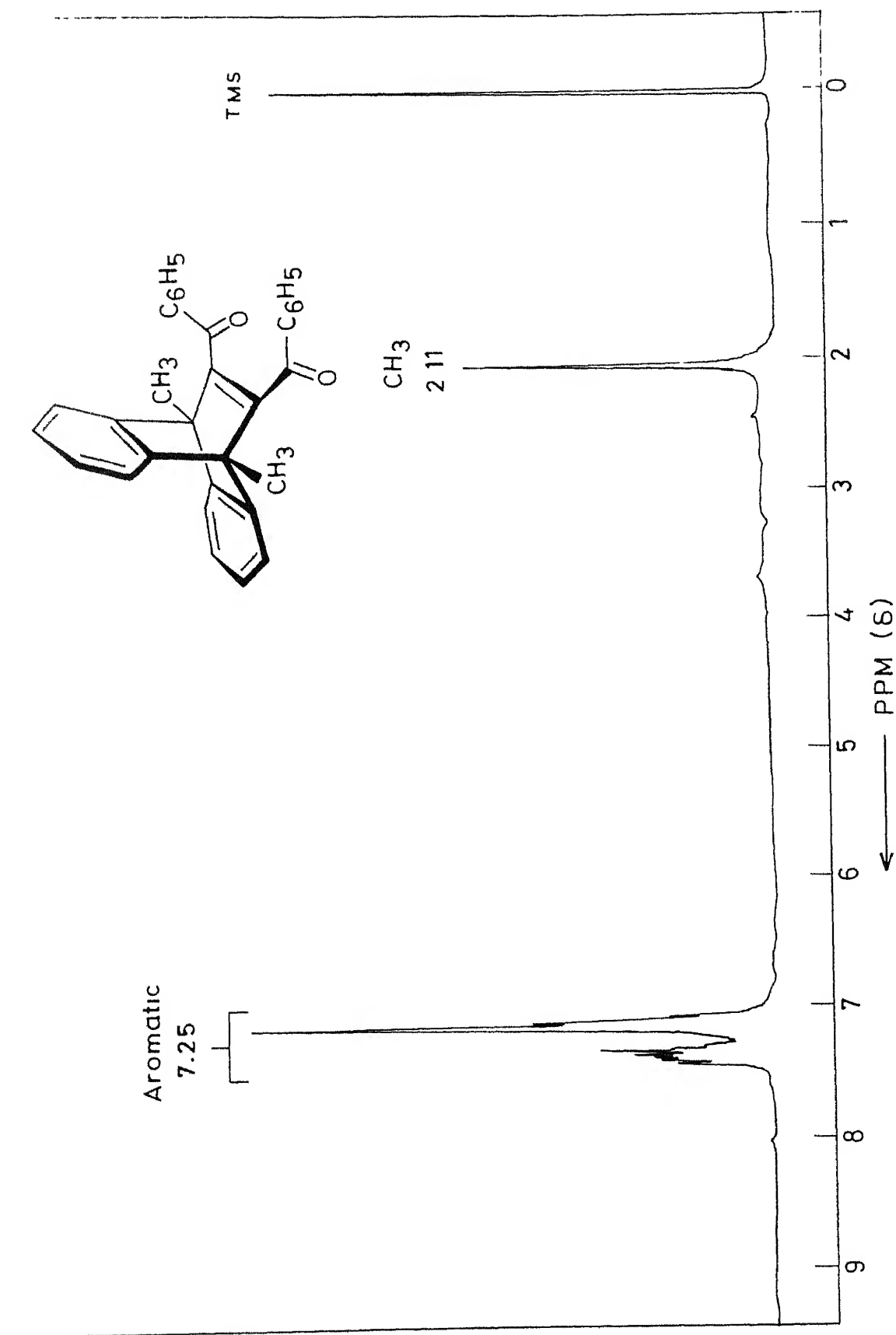


Fig. II 5 ^1H NMR spectrum (100 MHz) of 37.

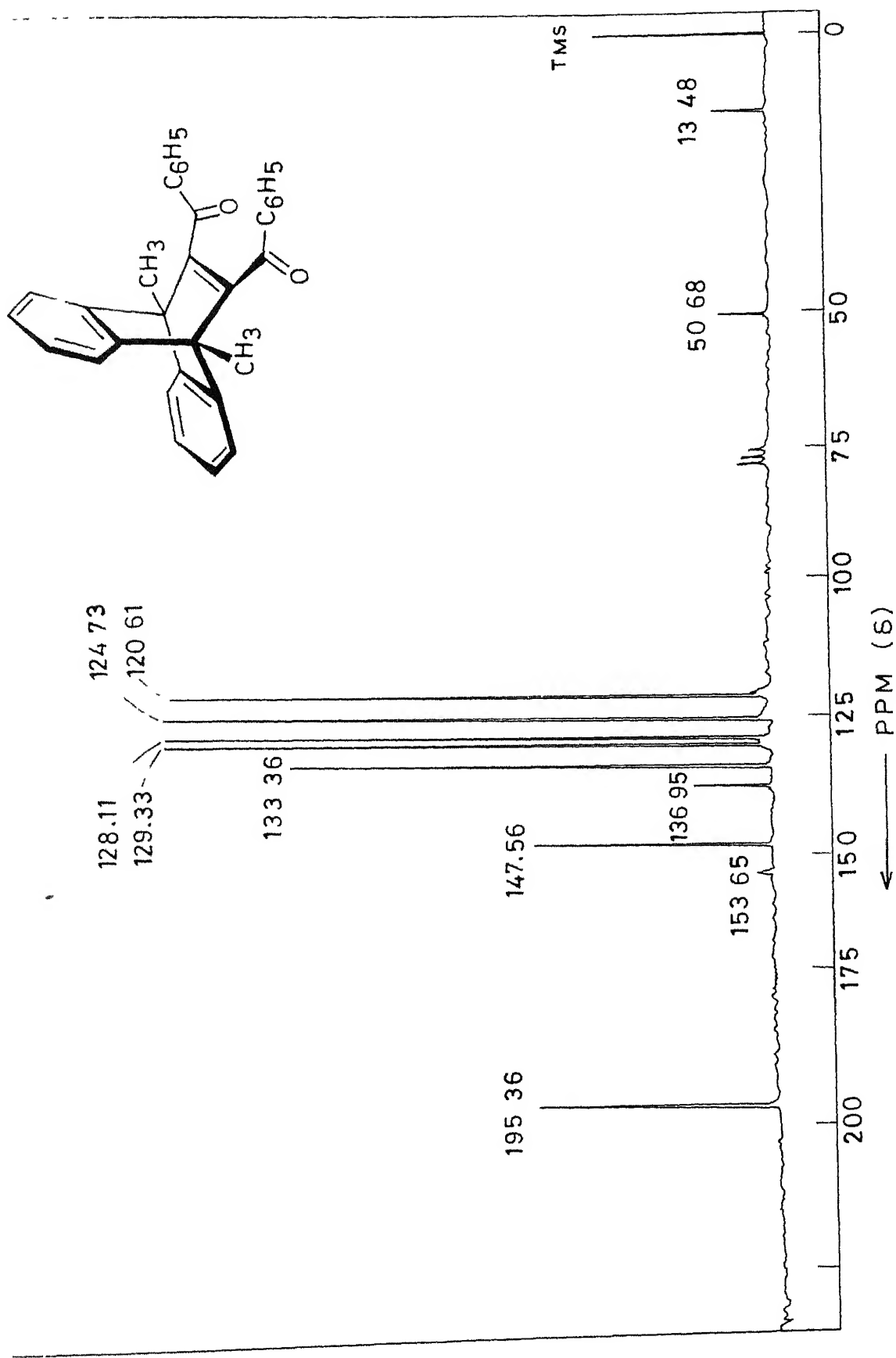


Fig II 6 ^{13}C NMR spectrum (25.2 MHz) of 37

and 37, which contain the cis-1,2-dibenzoylalkene functionality as part of the barrelene skeleton, one can in principle, expect two modes of phototransformations, namely, the di- π -methane rearrangement of the barrelene skeleton and the transformations of the dicarbonylalkene moiety. Preliminary studies⁴⁰ have shown that the irradiation of a benzene solution of 34, using a 450-W Hanovia medium-pressure mercury lamp for 4 hr gives a 88% yield of 1,2-dibenzoyldibenzotricyclo[3.3.0.0^{2,8}]octadiene (42). In the present studies, we have examined the phototransformations of 34-37, with a view to understanding the mode of reactions in these cases.

Irradiation of a methanol solution of 34, using a 450-W Hanovia medium-pressure mercury lamp for 1/2 hr gave a 52% yield of 42, along with a small amount (8%) of benzoic acid. In addition, 32% of the unchanged starting material (34) was also recovered from this reaction. When the irradiation of 34, however, was carried out in methanol, saturated with oxygen, for 1/2 hr, a 47% yield of 42 and a 22% yield of benzoic acid were obtained. In addition, 21% of the starting material (34) could also be recovered from this run. On the other hand, when the irradiation of 34 was carried out in acetone for 1/2 hr, a 89% yield of 42 was isolated.

With a view to examining whether oxygen quenches the photoisomerization reaction of 34, we have compared the irradiation reactions of benzene solutions of 34, employing a >340 nm

light source, under degassed and oxygen-saturated conditions. The progress of the reaction in each case has been monitored gas chromatographically and the results of these studies are summarized in Table II.1. Examination of Table II.1 reveals that the photoisomerization of 34 to 42 is inhibited to some extent through oxygen quenching of the excited state of 34.

It has been reported earlier⁴⁰ that the ^1H NMR spectrum of 42 shows a singlet at δ 4.24 (1 H) due to the methine proton of the cyclopropane ring and a second singlet at δ 4.64, assigned to the tertiary proton, attached to the five-membered rings. The aromatic protons have been observed as a complex multiplet, centred around δ 7.26 (18 H). The ^{13}C NMR spectrum of 42 (Fig. II.7) showed signals at δ 49.26, 58.19, 64.58 and 74.59 assigned to the C-8b, C-4b, C-8c and C-8d carbons, respectively. The signals at δ 194.25 and δ 196.73 have been assigned to the carbonyl carbons, whereas, the remaining sp^2 carbons appeared as twenty signals at δ 121.56, 121.89, 125.65, 126.14, 127.01, 127.20, 127.29, 127.69, 127.94, 128.47, 128.59, 130.02, 132.68, 133.18, 135.35, 135.57, 136.78, 137.09, 149.77 and 150.51.

With a view to finding out whether the cyclopropane ring in 42 is easily cleaved under hydrogenation conditions, we have examined the catalytic hydrogenation of 42, under controlled conditions. Catalytic hydrogenation of 42 using 5% Pd on charcoal in THF gave a 60% yield of 9a,10-dibenzoyl-4b,9,9a,10-tetrahydro-cis-indeno[1,2-a]indene (41). The ^1H NMR

Table II.1 Photoisomerization of 34 to 42 in benzene under different conditions^{a,b}

Run #	Time (Minutes)	Conditions	Starting material (<u>34</u>) (%) ^c	Product (<u>42</u>) (%) ^c
1	0	Degassed solution	99.9'	0
2	5	Degassed solution	92.6	6.9
3	15	Degassed solution	69.1	28.7
4	30	Degassed solution	43.9	53.7
5	15	O ₂ -saturated solution	96.8	3.1
6	30	O ₂ -saturated solution	86.8	9.2

- a) A solution of 34 (4.199×10^{-3} M) in benzene was used for these runs.
- b) Irradiations were carried out using a > 345 nm light source.
- c) The yields were determined gas chromatographically.

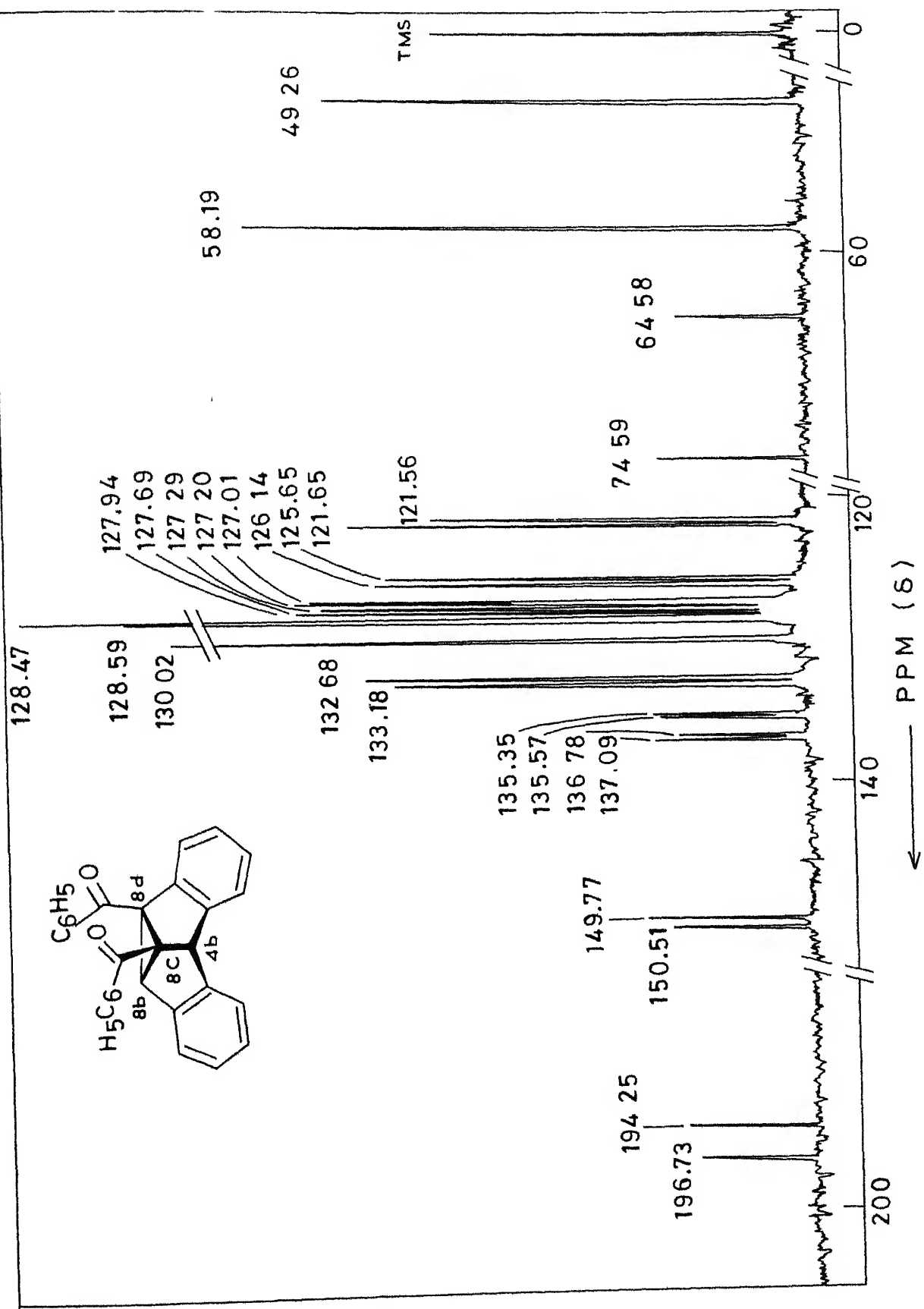


Fig II.7 ^{13}C NMR spectrum (67.89 MHz) of 42.

spectrum of 41 (Fig. II.8), for example, showed two doublets at δ 3.55 (1 H, $J_{g,g'} = 17$ Hz) and 3.79 (1 H, $J_{g,g'} = 17$ Hz), which have been assigned to the two methylene protons at C-9 position. In addition, the spectrum showed two singlets at δ 5.69 (1 H) and 5.87 (1 H), which have been assigned to the H-4b and H-11 protons, respectively. The aromatic protons appeared as two complex multiplets centred around δ 7.29 (14 H) and 7.87 (4 H), respectively. The ^{13}C NMR spectrum of 41 (Fig. II.9) showed signals at δ 44.33, 59.30, 62.87 and 70.03, which have been assigned to the C-8b, C-4b, C-8d and C-8c carbons, respectively. The carbonyl carbons showed signals at δ 198.87 and 200.76, respectively, whereas the remaining sp^2 carbons appeared at δ 123.97, 124.50, 125.12, 125.68, 127.04, 127.10, 127.66, 128.25, 128.34, 128.62, 128.84, 131.79, 133.18, 136.47, 136.84, 138.67, 139.66, 143.94 and 145.46.

A probable route to the formation of 42 in the photoisomerization of 34 is shown in Scheme II.8. It is assumed that the excited triplet state of 34 leads initially to the diradical intermediate 38, through a benzo-vinyl bridging. Subsequent transformation of 38 leads to 42, presumably through a second diradical intermediate 39. The exact pathway for the formation of small amounts of benzoic acid in the irradiation of 34 in presence of oxygen is still not clear. One of the possible pathways may involve the initial formation of a dioxetane intermediate 40, which will,

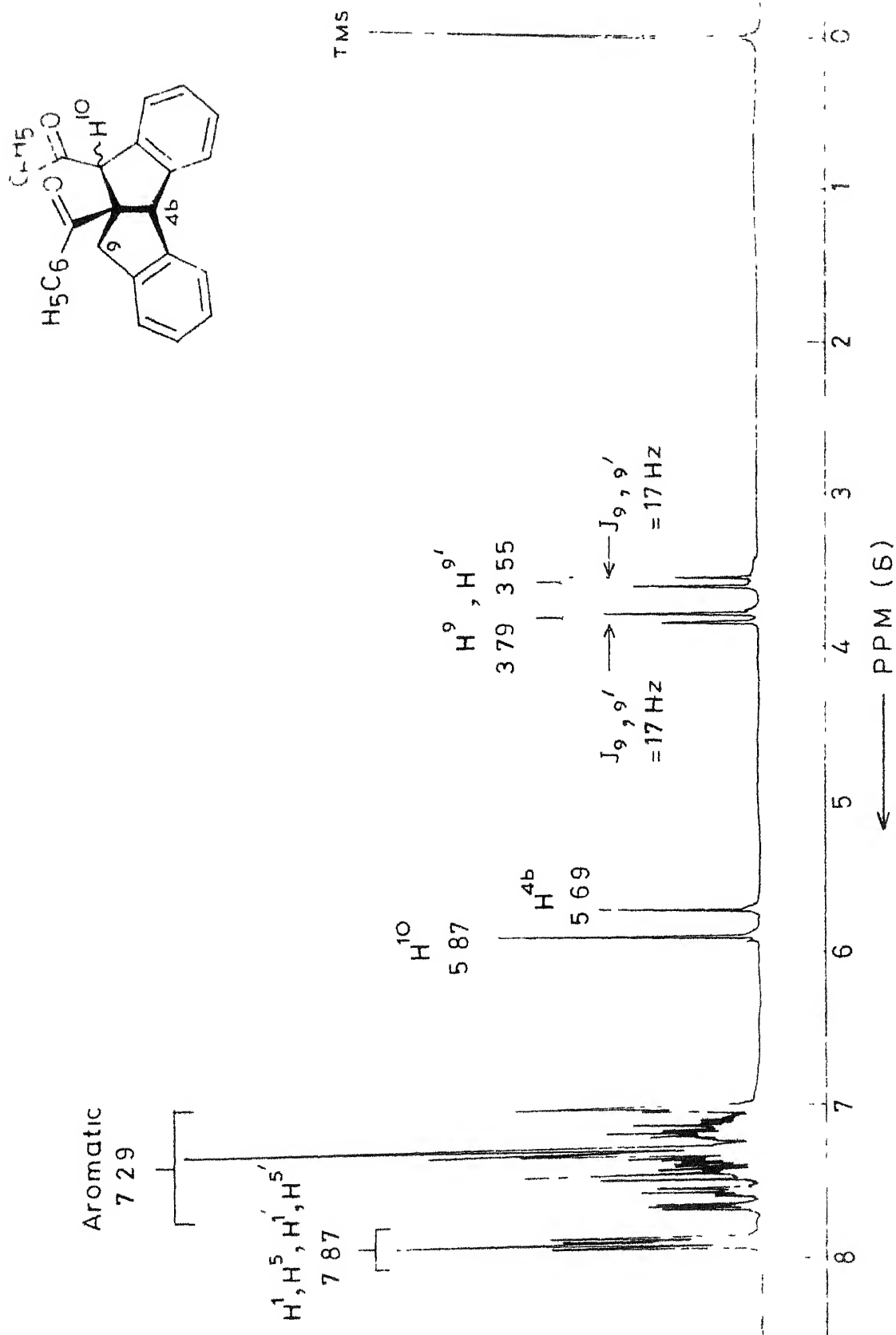


Fig II 8 ¹H NMR spectrum (270 MHz) of 41.

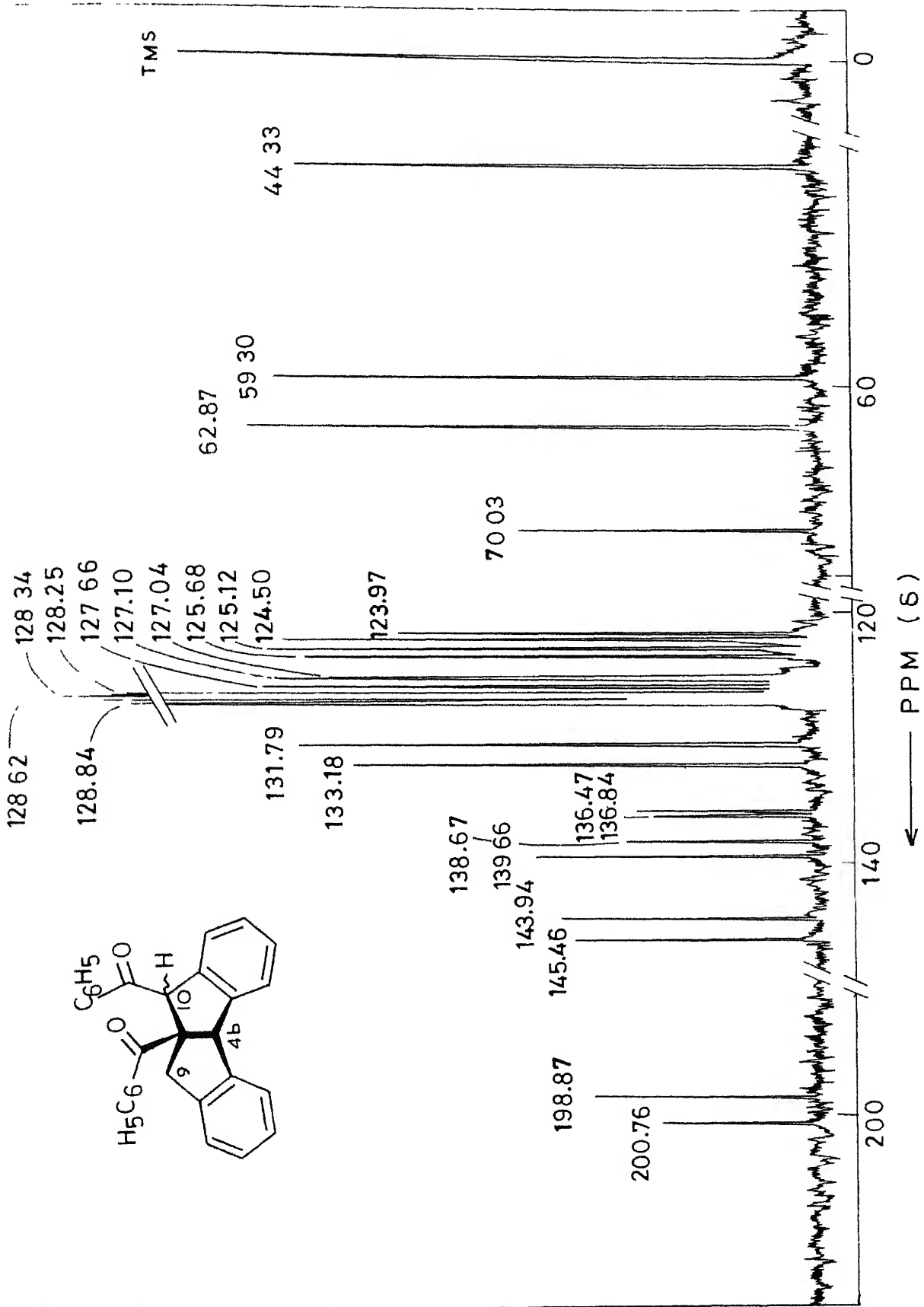
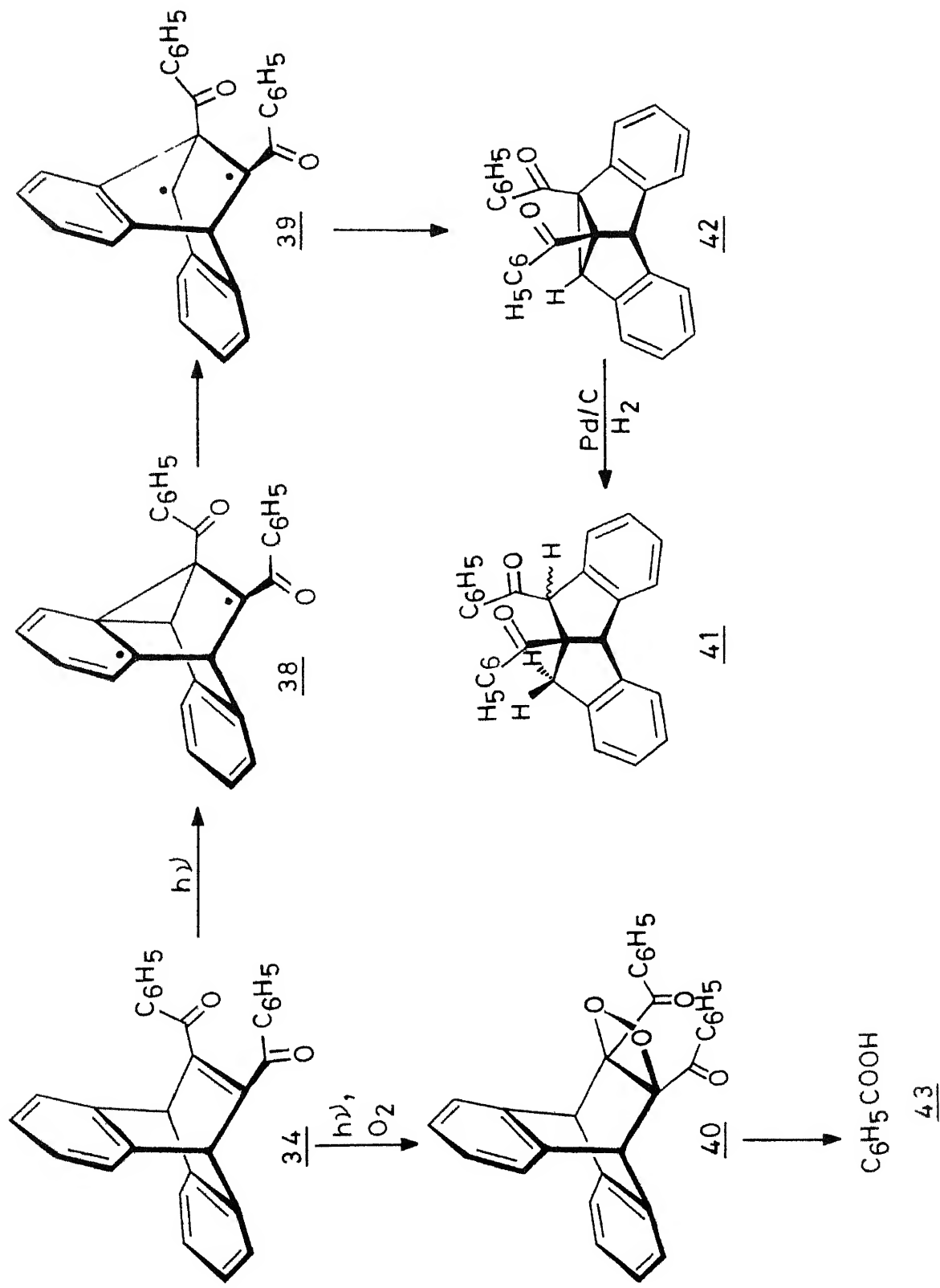


Fig. II. 9 ¹³C NMR spectrum (67.89 MHz) of 41



subsequently, undergo fragmentation to benzoic acid, under the reaction conditions. An analogous dioxetane intermediate has been invoked in the photooxygenation of tetraphenyl-*p*-dioxin.⁵⁰

Irradiation of the unsymmetrically substituted dibenzo-barrelene, 11,12-dibenzoyl-9,10-dihydro-9-methyl-9,10-etheno-anthracene (35) in benzene for 1/2 hr gave a 54% yield of 8c,8d-dibenzoyl-4b,8b,8c,8d-tetrahydro-4b-methyldibenzo[a,b]cyclopropa[c,d]pentalene (47) and a small amount (12%) of benzoic acid. Similarly, the irradiation of 35 in methanol gave a 50% yield of 47 and a 8% yield of benzoic acid, whereas the irradiation in acetone, under analogous conditions, gave a 64% yield of 47 and a 8% yield of benzoic acid. Table II.2 summarizes the results of our studies on the irradiation of 35 under different conditions, wherein the product formation has been monitored gas chromatographically. It is evident from Table II.2, that oxygen quenches the photoisomerization of 35 to some extent, as in the case of 34.

The structure of 47 was arrived at on the basis of analytical results, spectral data and chemical evidences. The ¹H NMR spectrum of 47 (Fig. II.10), for example, showed a sharp singlet at δ 1.74 (3 H), assigned to the bridgehead methyl group and a second singlet at δ 4.62 (1 H), assigned to the methine proton of the cyclopropane ring. The aromatic hydrogens appeared as a complex multiplet centred around δ 7.30 (18 H). The ¹³C NMR spectrum of 47 (Fig. II.11) showed

Table II.2 Photoisomerization of 35 to 47,
under different conditions^{a, b}

Run #	Time (Minutes)	Solvent	Conditions	Starting material (<u>35</u>) (%) ^c	Product <u>47</u> (%) ^c
1	0	Benzene	Degassed	99.3	0
2	15	Benzene	Degassed	23.0	59.5
3	30	Benzene	Degassed	5.0	71.6
4	15	Benzene	O ₂ -saturated	88.9	7.6
5	30	Benzene	O ₂ -saturated	69.9	19.5
6	0	Acetone	Degassed	99.1	0
7	15	Acetone	Degassed	43.6	36.9
8	30	Acetone	Degassed	16.3	54.4

a) Solution of 35 in benzene (9.706×10^{-3} M) and acetone (8.349×10^{-3} M) were used for these runs.

b) Irradiations were carried out using a > 345 nm light source.

c) The yields were determined gas chromatographically.

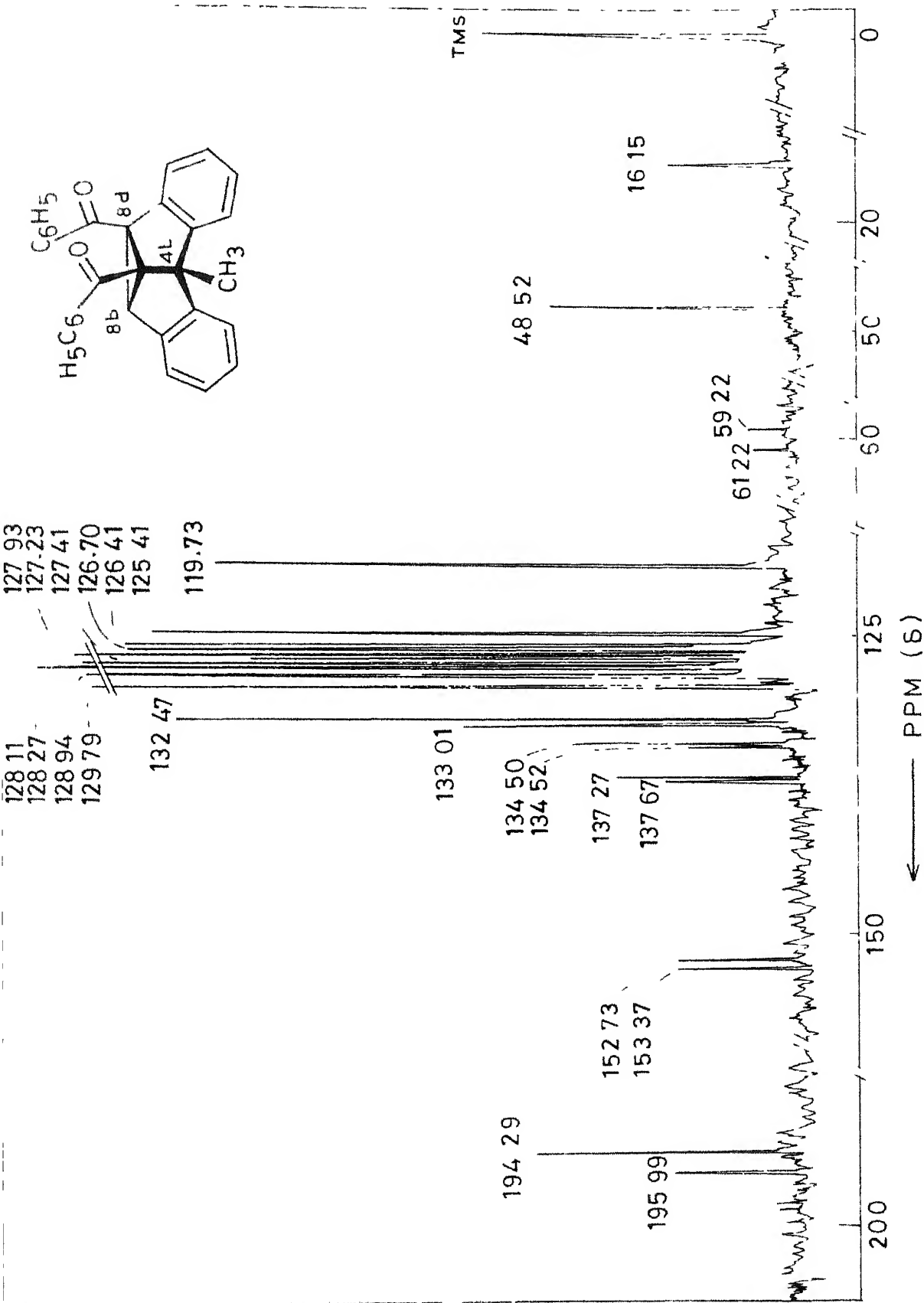


Fig II 11 ¹³C NMR spectrum (25.2 MHz) of 47

signals at δ 16.15, 48.52, 59.22 and 61.22, assigned to the methyl carbon and C-8b, C-4b and C-8c carbons, respectively. The carbonyl carbon signals appeared at δ 194.29 and 195.99, respectively, whereas the other sp^2 carbons appeared at δ 119.73, 125.41, 126.41, 126.70, 127.23, 127.41, 127.93, 128.11, 128.27, 128.94, 129.79, 132.47, 133.01, 134.50, 134.52, 137.27, 137.67, 152.73 and 153.37.

The mass spectrum of 47 (Fig. II.12) showed a molecular ion peak at m/e 426 (52), whereas other prominent peaks were observed at m/e 321 (66), 306 (7), 293 (35), 278 (5), 276 (28), 243 (13), 216 (8), 215 (19), 201 (10), 200 (11), 105 (100), 97 (12), 95 (10), 85 (12), 83 (15), 81 (13), 77 (68), 71 (25), 69 (25), 57 (18), 55 (34) and 51 (14). Some of the probable fragmentation modes are shown in Scheme II.9. One of the fragmentation modes of 47 involves the loss of a benzoyl group to give 47b at m/e 321, which in turn can lose either carbon monoxide to give 47c at m/e 293 or a second benzoyl group to give 47e at m/e 216. The fragment 47c, for example, can lose a methyl group to give 47f at m/e 278, which in turn can lose two hydrogen atoms to give 47i at m/e 276. Likewise, the fragment 47e can lose a methyl group to give 47h at m/e 201.

Further confirmation of the structure of 47 was derived from hydrogenation studies. Catalytic hydrogenation of 47 over 5% Pd on charcoal in THF, gave a product, identified as cis-9a,10-dibenzoyl-4b,9,9a,10-tetrahydro-4b-methyl-cis-indeno[1,2-a]indene (50). The structure of 50 has been

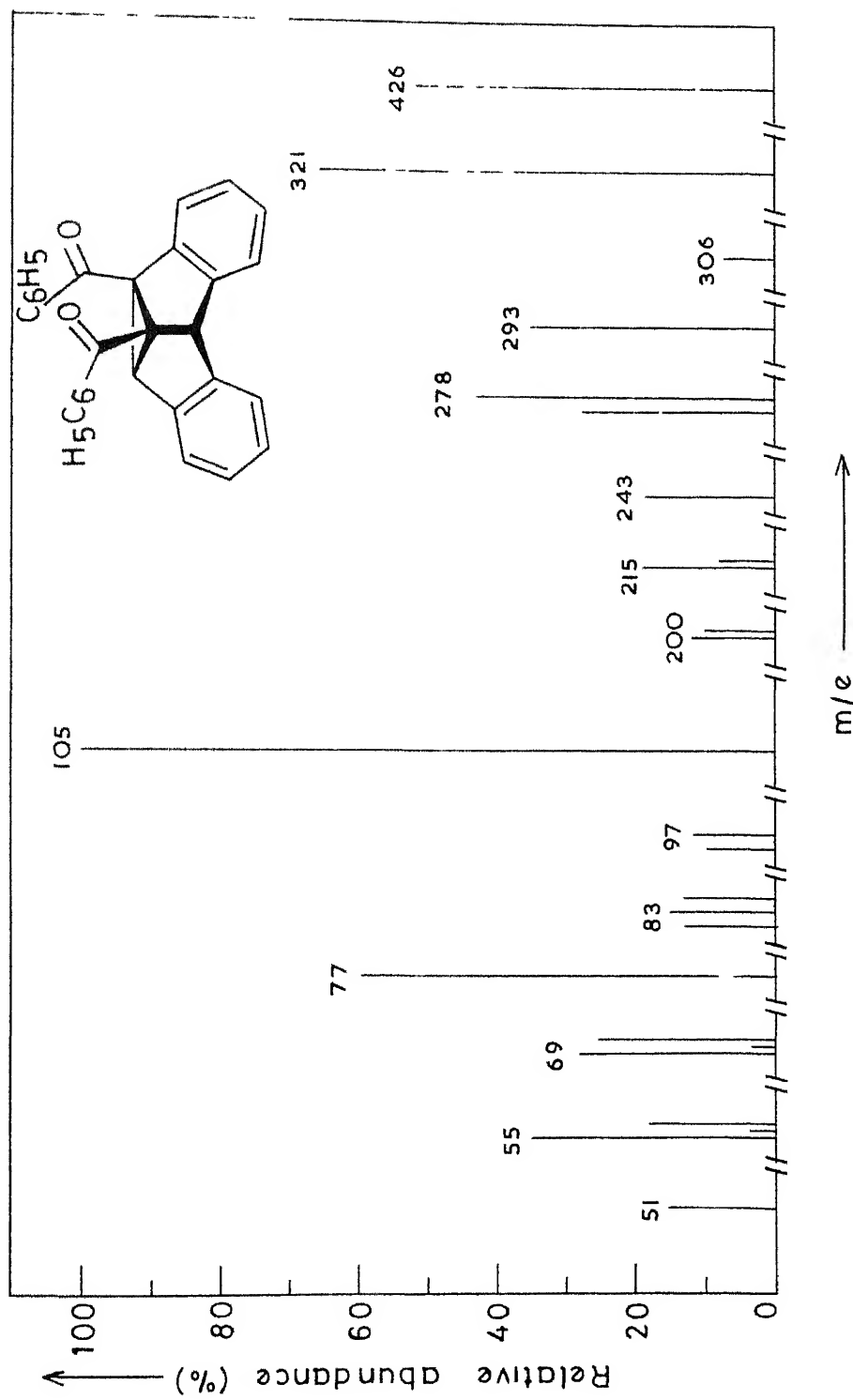
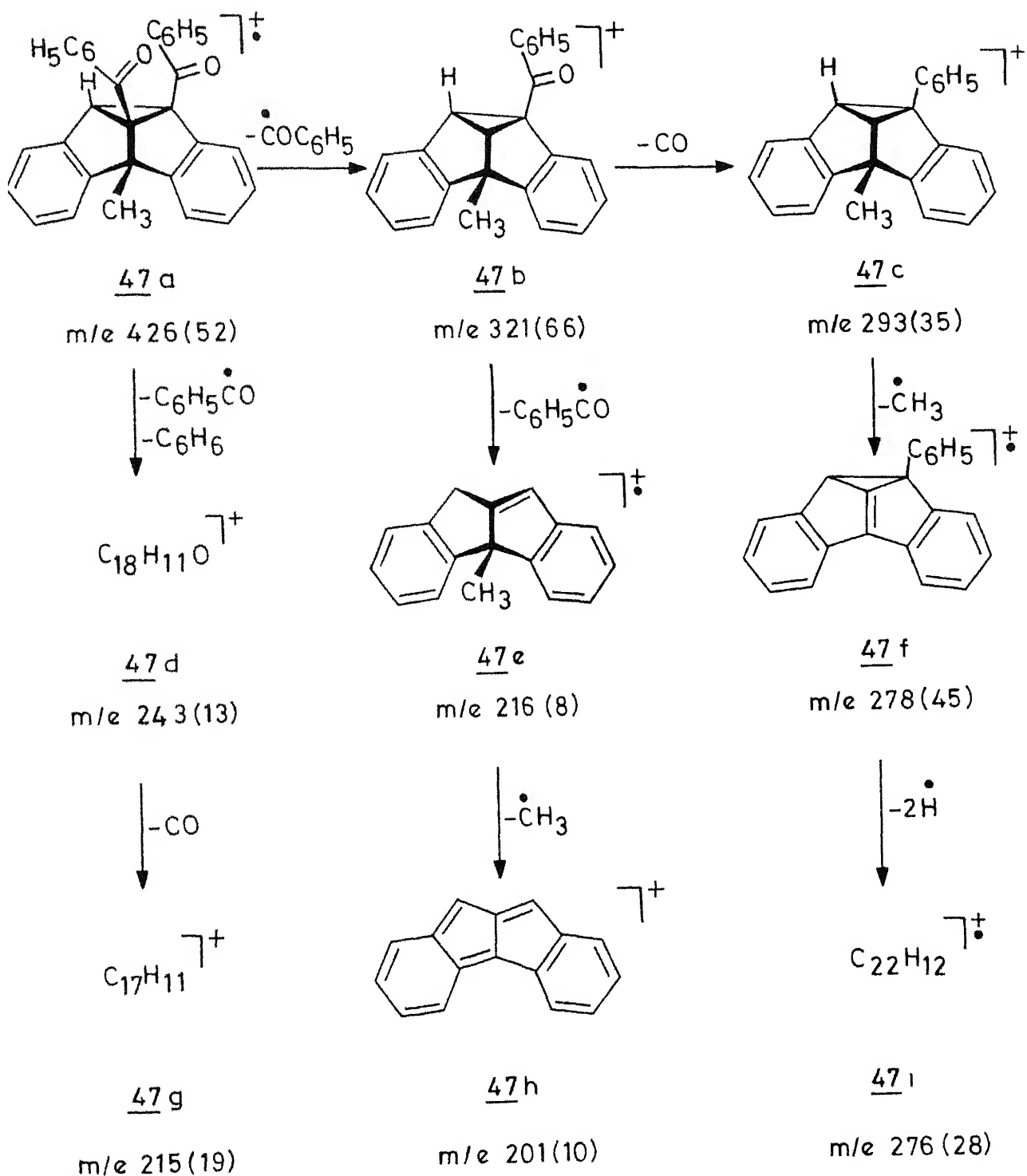


Fig II.12 Mass spectrum of 47.

Scheme II.9



arrived at, on the basis of analytical results and spectral data. The ^1H NMR spectrum of 50 (Fig. II.13), for example, showed a singlet at δ 1.69 (3 H) due to the methyl group at C-4b position and a second singlet at δ 6.37 (1 H) due to the methine proton at C-10 position. In addition, the spectrum showed two doublets at δ 3.09 (1 H, $J_{9,9'} = 18$ Hz) and 3.32 (1 H, $J_{9,9'} = 18$ Hz), respectively, due to the geminal hydrogens H-9 and H-9'. The aromatic protons appeared as a complex multiplet centred around δ 7.25 (18 H). It might be pointed out here that if the structure of the photoproduct were to be represented by 48, wherein the methyl group is at C-8b position, then 49 would have resulted as the hydrogenation product and the ^1H NMR results are not in agreement with this possibility (Scheme II.10).

The exclusive formation of 47 in the photoisomerization of 35 would suggest that of the two possible pathways involving the diradicals 44 and 46, arising through an initial benzo-vinyl bridging, path 'a', involving 44 seems to be preferred (Scheme II.10). The formation of small amounts of benzoic acid in the irradiation of 35 in presence of air or oxygen could perhaps arise through a dioxetane intermediate, as in the case of 34.

In continuation of our studies, we have examined the phototransformations of 11,12-dibenzoyl-9,10-dihydro-9-hydroxy-9,10-ethenoanthracene (36). Irradiation of a benzene

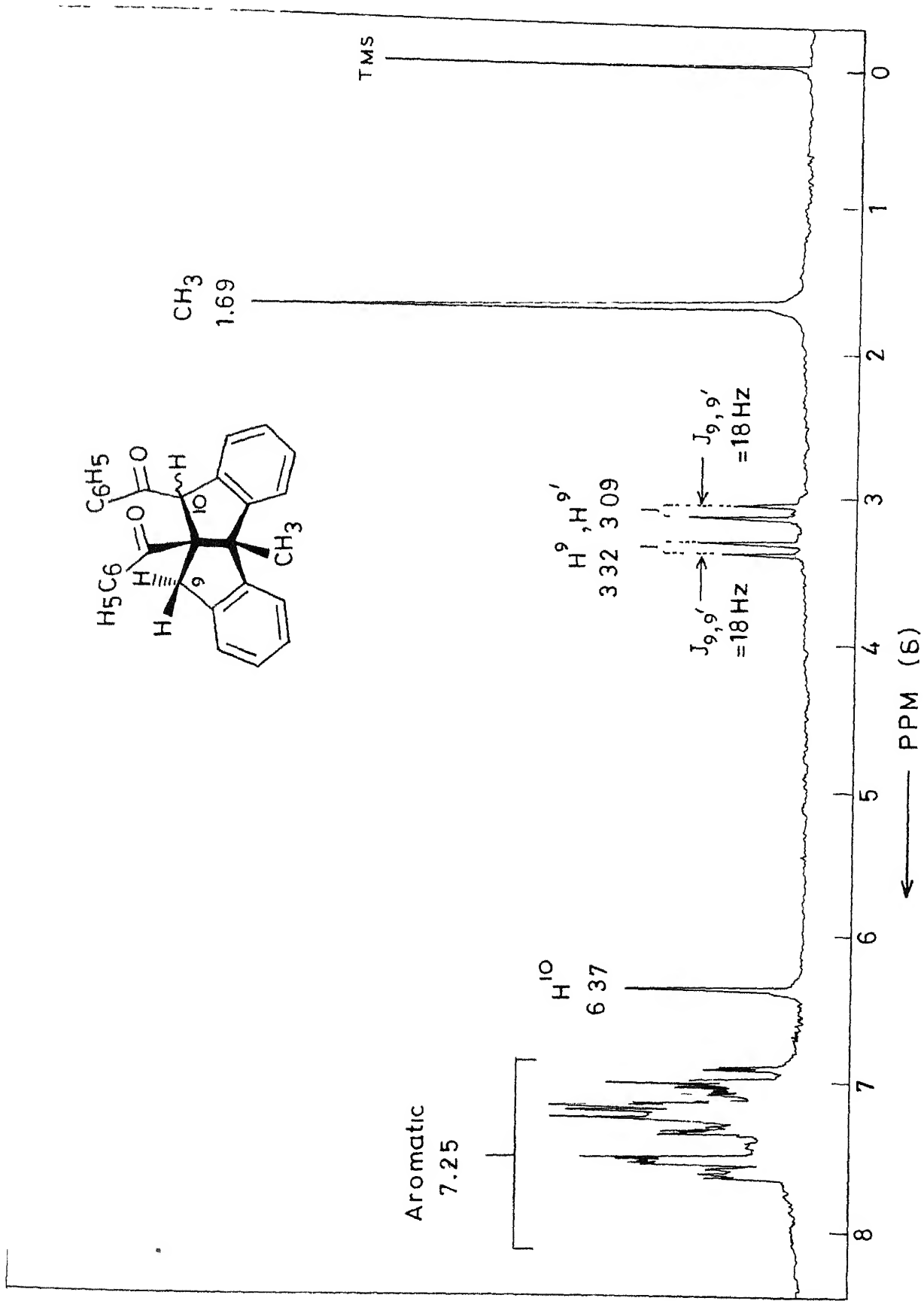
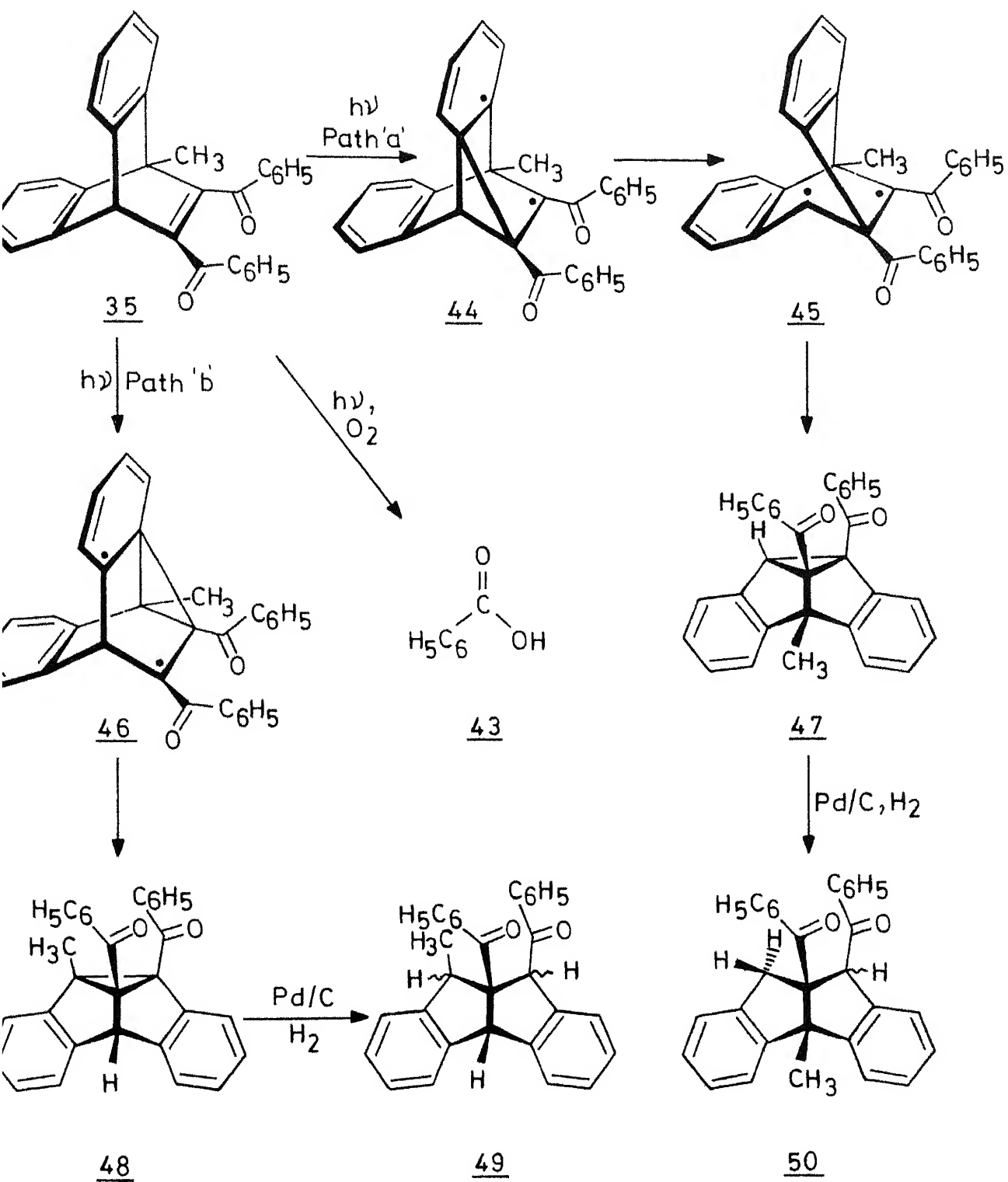


Fig. II 13 ^1H NMR spectrum (270 MHz) of 50.

Scheme II.10



solution of 36 for 1 hr gave a 26% yield of 9a,10-dibenzoyl-4b,9,9a,10-tetrahydro-9-oxo-cis-indeno[1,2-a]indene (55), along with a small amount (4%) of benzoic acid. In addition, 50% of the unchanged starting material (36) could also be recovered from this reaction. Irradiation of an acetone solution of 36 for 1 hr, on the other hand, gave a 62% yield of 55, along with a 7% yield of benzoic acid. The structure of 55 was arrived at on the basis of analytical results and spectral data. The ^1H NMR spectrum of 55 (Fig. II.14), for example, showed two singlets at δ 5.85 (1 H) and 6.33 (1 H), assigned to H-4b and H-10 protons, respectively. These assignments are in agreement with the reported values for proton positions in a compound such as cis-indeno[1,2-a]-indanone, containing protons under similar environment.³⁸ In addition, the aromatic protons appeared as a complex multiplet centred around δ 7.55 (18 H).

The ^{13}C NMR spectrum of 55 (Fig. II.15) showed several signals at δ 56.42, 58.15, 82.02, 125.40, 125.72, 127.67, 132.31, 133.67, 135.90, 136.40, 137.30, 138.90, 143.20, 157.65, 192.58, 197.73 and 201.60. In addition, several overlapping signals were observed in the region δ 128.38-129.16. The signals at δ 56.42, 58.15 and 82.02 were assigned to C-4b, C-10 and C-9a, respectively. The signals due to C-4b and C-10 appeared as doublets, whereas the signal due to C-9a appeared as a singlet, in the coupled spectrum. The signals at δ 192.58, 197.73 and

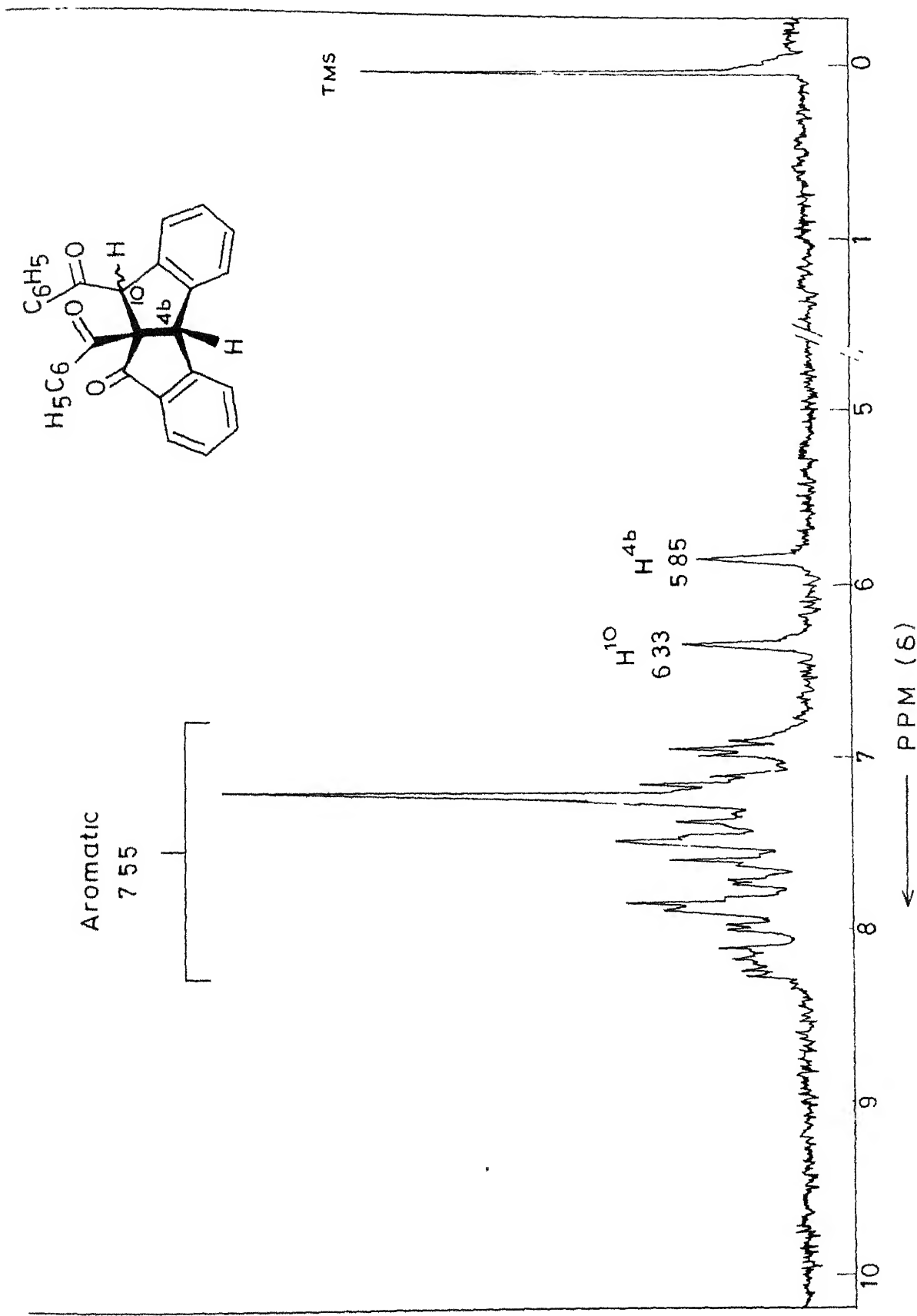


Fig II 14 ¹H NMR spectrum (90 MHz) of 5f

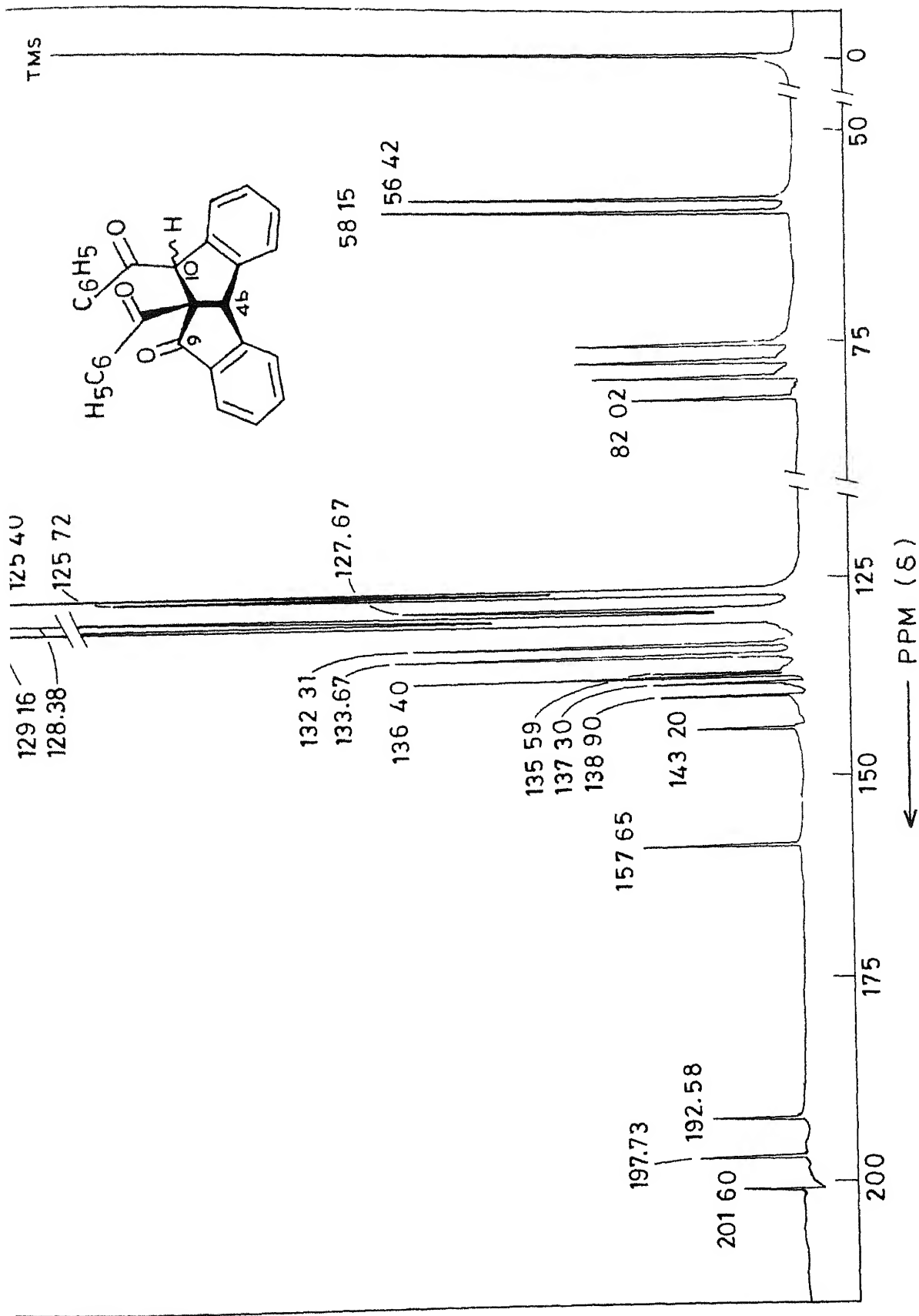


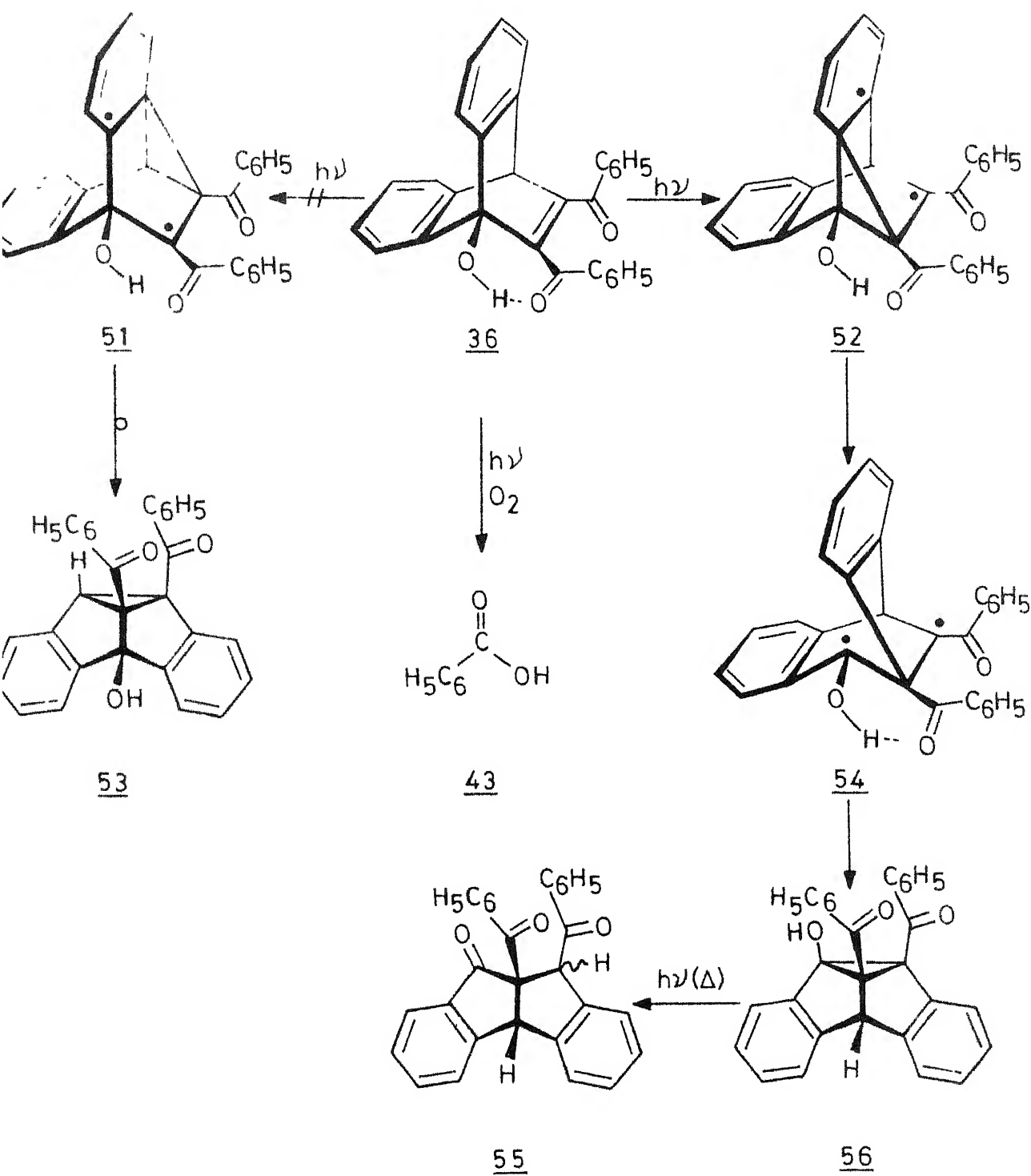
Fig II . 15 ^{13}C NMR spectrum (15.08 MHz) of 55

201.60 were assigned to the three carbonyl carbons of 55, whereas the signals between δ 125.40 and 157.65 have been assigned to the remaining sp^2 carbons.

A probable route to the formation of 55 in the photoisomerization of 36 is shown in Scheme II.11. Of the two diradical intermediates which could arise through an initial benzo-vinyl bridging of the triplet excited state of 36, the one in which both the hydrogen bonding possibility of the hydroxyl group with an adjacent carbonyl group and a proper delocalization of the radical centre exists, as in 52, seems to be the preferred intermediate. The diradical species 52, can in turn undergo transformation to a new diradical species 54, which will then give rise to the hydroxysemibullvalene derivative 56. A subsequent photo-transformation of 56 would result in the formation of the triketo derivative 55, as shown in Scheme II.11.

In contrast to the photoisomerizations of the dibenzobarrelenes 34-36, the phototransformations of 11,12-dibenzoyl-9,10-dihydro-9,10-dimethyl-9,10-ethenoanthracene (37) gave rise to a variety of products, depending on the reaction conditions. Irradiation of 37 in methanol for $\frac{1}{4}$ hr, for example, gave a mixture of products consisting of 2,3-dibenzoyl-2,3-dihydro-1,4-dimethyl-2-benzonaphthalene (60, 25%), 1,4-dibenzoyl-5,8-dimethyl-2,6-dibenzocyclooctatetraene (57, 27%) and benzoic acid (8%). In addition, 17% of the

Scheme II 11



unchanged starting material (37) could also be recovered from this reaction. Irradiation of a benzene solution of 37 for 1/2 hr, on the other hand, gave a mixture of products consisting of the carbinol derivative 63 (45%), 60 (12%), 57 (20%) and benzoic acid (7%). In contrast, the irradiation of an acetone solution of 37 for 1/2 hr gave a 80% yield of an indeno[1,2-a]-indene derivative 65 and a 9% yield of benzoic acid.

The structures of the different products such as 60, 57, 63 and 65, formed in the phototransformations of 37 have been established on the basis of analytical results, spectral data and chemical evidences. The ^1H NMR spectrum of 60 (Fig. II.16), for example, showed a singlet at δ 1.77 (6 H), assigned to the methyl protons, whereas the olefinic protons appeared as a complex multiplet, centred around δ 6.82 (4 H). The aromatic protons appeared as a multiplet centred around δ 7.36 (14 H). The ^{13}C NMR spectrum of 60 (Fig. II.17) showed several signals at δ 22.88, 60.59, 120.39, 123.58, 126.42, 127.79, 127.91, 131.89, 136.69, 137.45, 153.59, 154.58 and 199.78. Of these, the signal at δ 22.88 has been assigned to the methyl carbons, whereas the signal at δ 60.69 could be assigned to the C-2 and C-3 carbons, which are considerably deshielded due to the attachment of benzoyl groups.^{47,48} The signal due to the carbonyl carbons appeared at δ 199.78, whereas the signals between δ 120.39-154.58 could be assigned to the other sp^2 carbons present in 60.

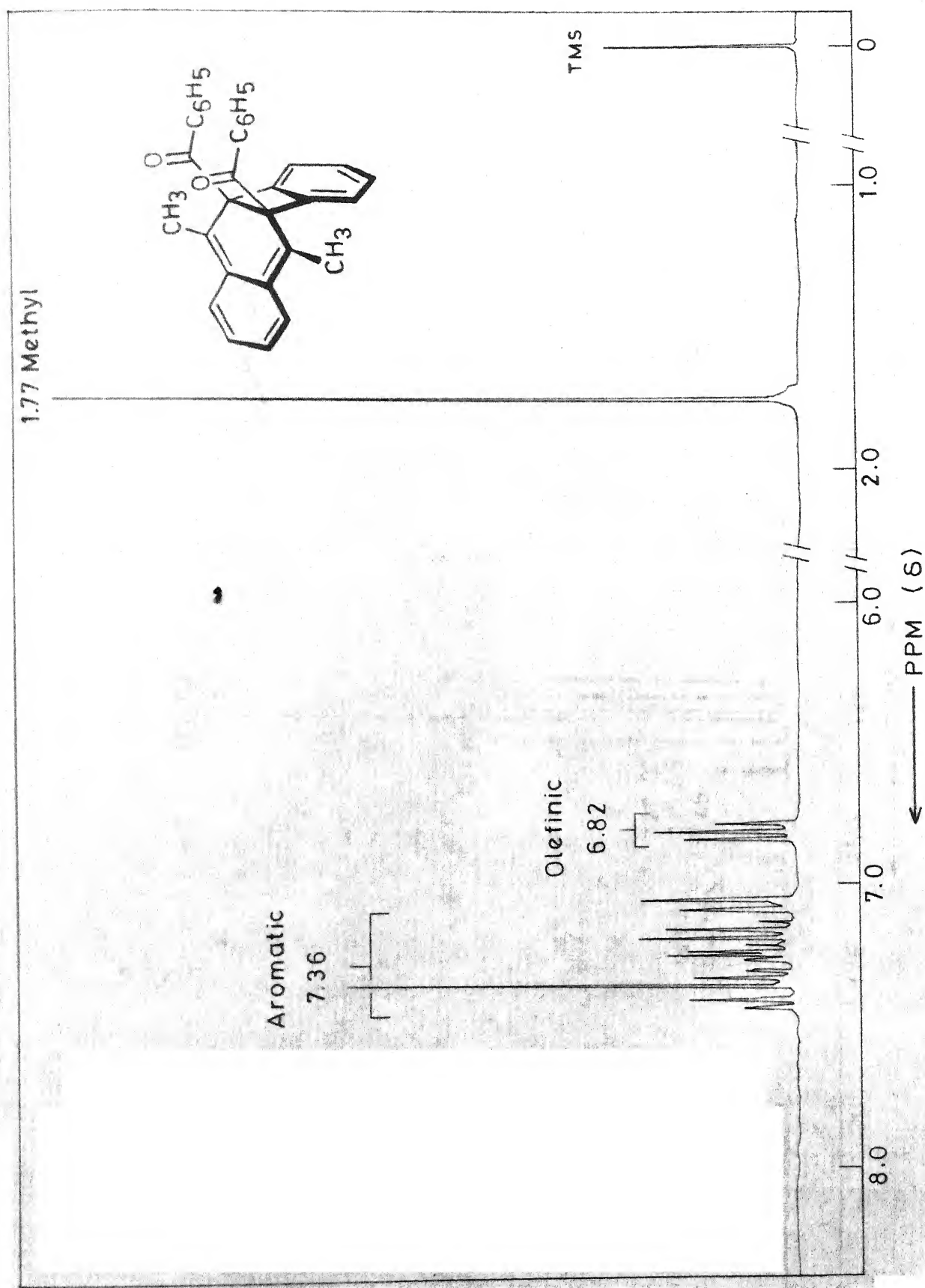


Fig. II.16 ^1H NMR (270 MHz) spectrum of 60.

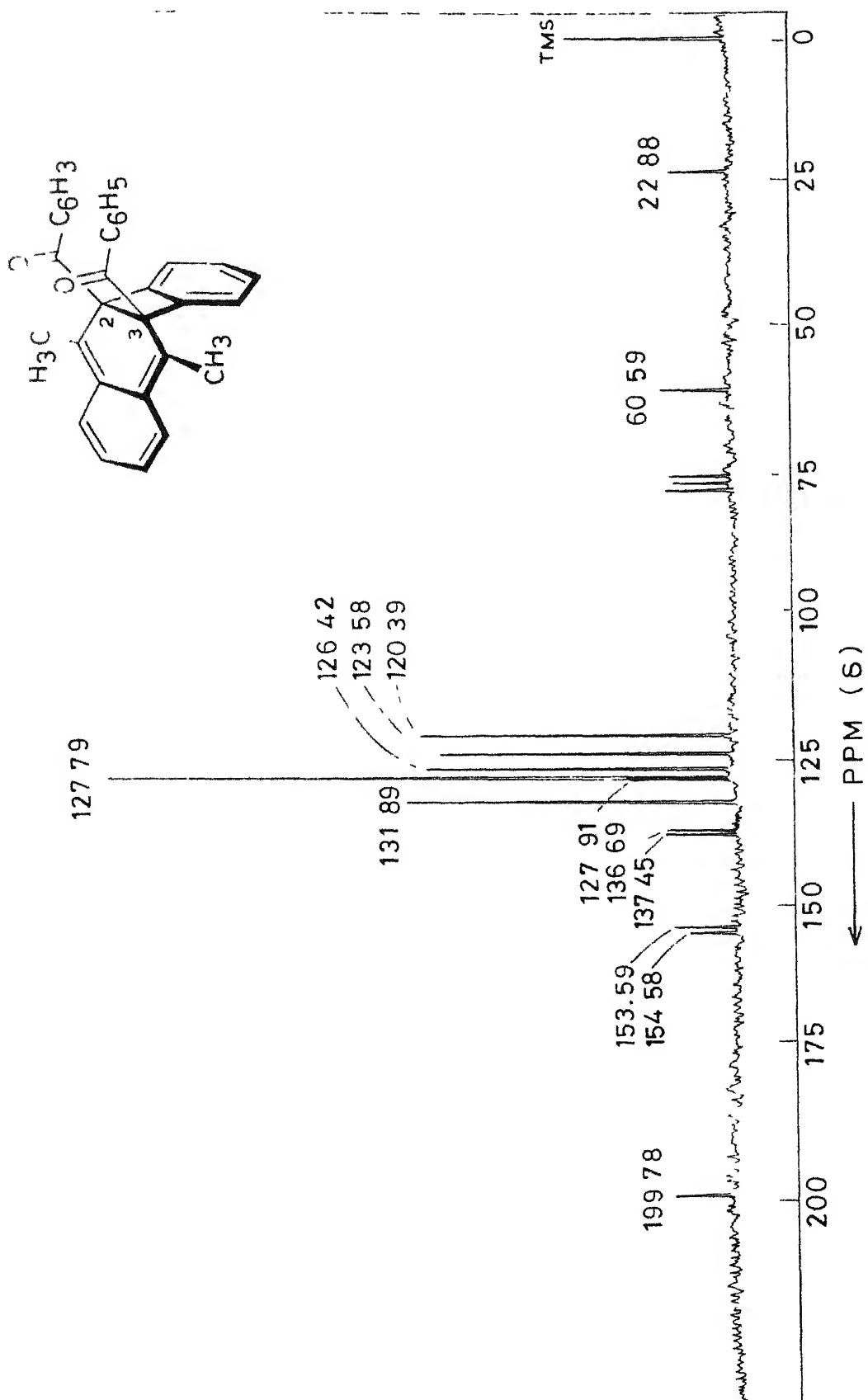


Fig. II 17 ^{13}C NMR spectrum (25.2 MHz) of 60

The mass spectrum of 60 (Fig. II.18) showed a molecular ion peak at m/e 440 (100). Other peaks in the spectrum were observed at m/e 335 (4), 320 (97), 290 (5), 231 (25), 230 (90), 228 (45), 226 (35), 215 (98), 213 (18), 202 (10), 201 (8), 200 (5), 189 (8), 105 (98), 78 (50), 77 (83), 62 (21), 57 (20), 56 (8), 55 (18), 52 (22), 51 (30) and 43 (15). Some of the probable fragmentation modes are shown in Scheme II.12. It is reasonable to assume that the molecular ion of 60 loses a benzoyl group to give the fragment 60b at m/e 335, which in turn can lose either a methyl group to give 60c at m/e 320 or a second benzoyl group to give 60e at m/e 230. The loss of a methyl group from 60f would give rise to 60h at m/e 200, whereas the loss of two hydrogen atoms from 60e would result in 60g at m/e 228.

The ^1H NMR spectrum of 1,4-dibenzoyl-5,8-dimethyl-2,6-dibenzocyclooctatetraene (57) (Fig. II.19), for example, showed a singlet at δ 2.09 (6 H), due to the methyl protons, whereas, the aromatic protons appeared as two sets of complex multiplets, centred around δ 7.30 (14 H) and 8.27 (4 H). The ^{13}C NMR spectrum of 57 (Fig. II.20) showed several signals at δ 23.15, 126.86, 127.11, 127.47, 127.60, 128.68, 129.63, 133.42, 135.17, 136.40, 138.39, 138.97, 141.77 and 197.81. Of these, the signal at δ 23.15 has been assigned to the methyl carbons, whereas the one at δ 197.81 has been assigned to the carbonyl carbons. The remaining signals between δ 126.86 and 141.77 could be assigned to the other sp^2 carbons in 57.

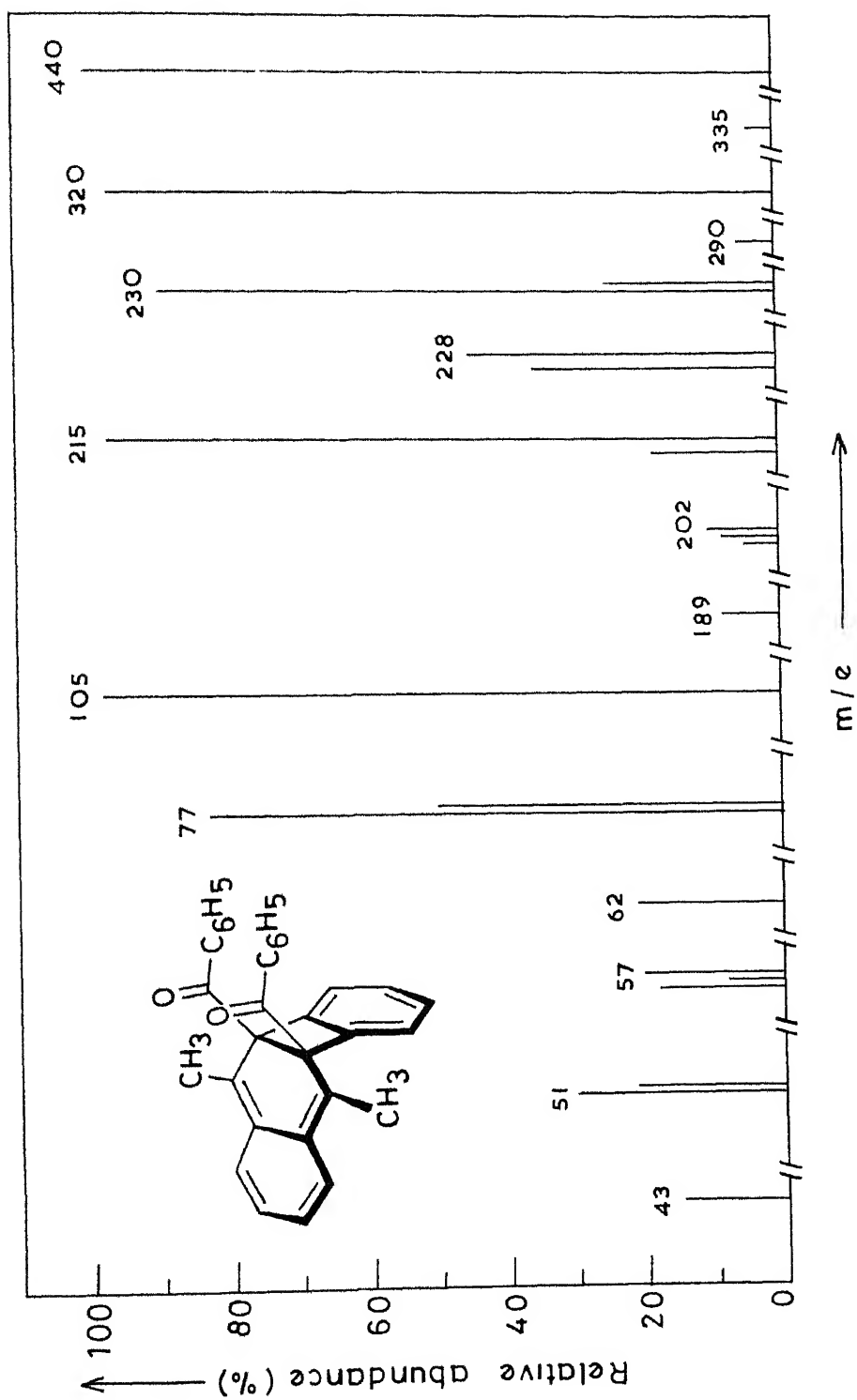
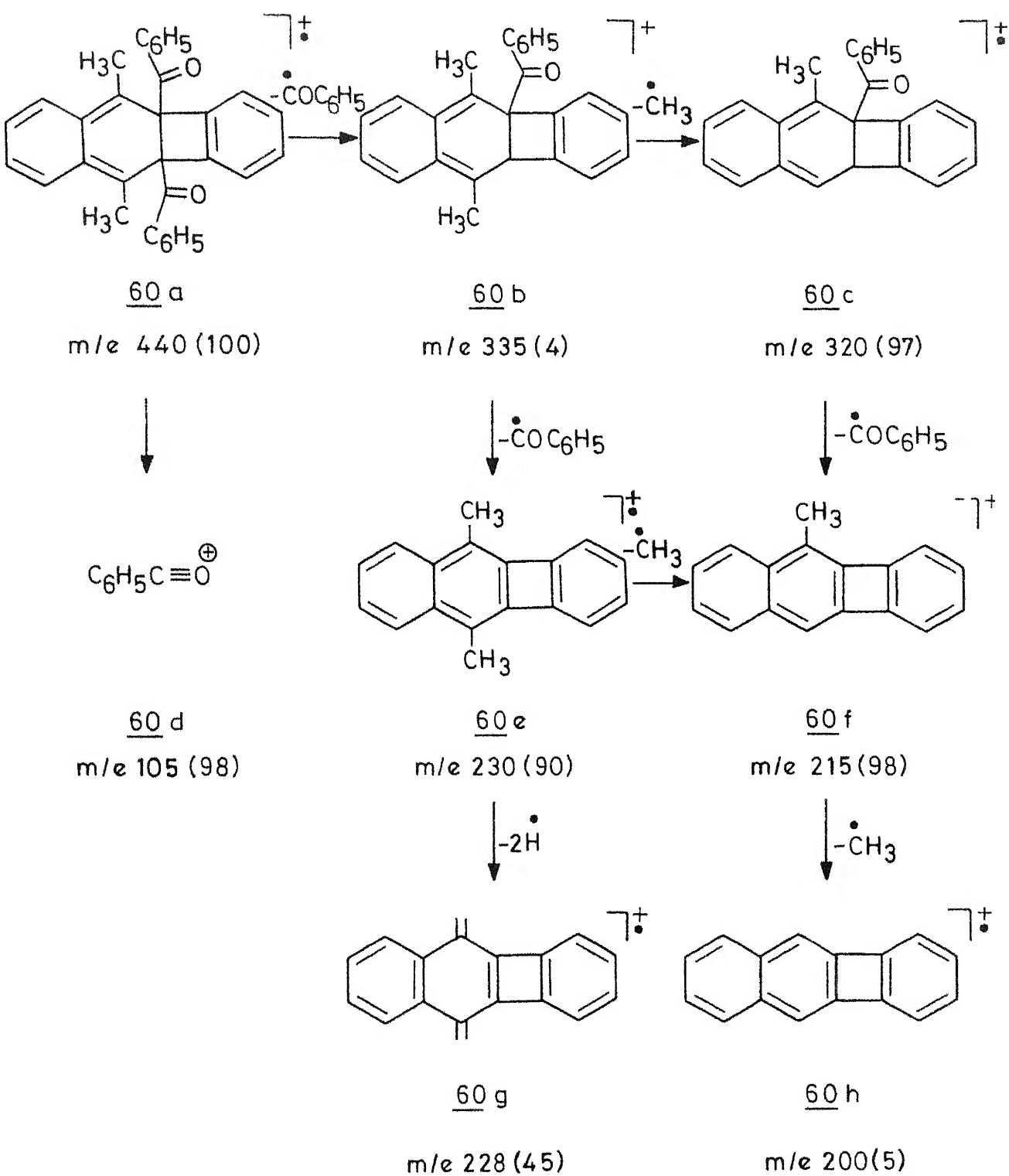


Fig. II.18 Mass spectrum of 60.

Scheme II 12



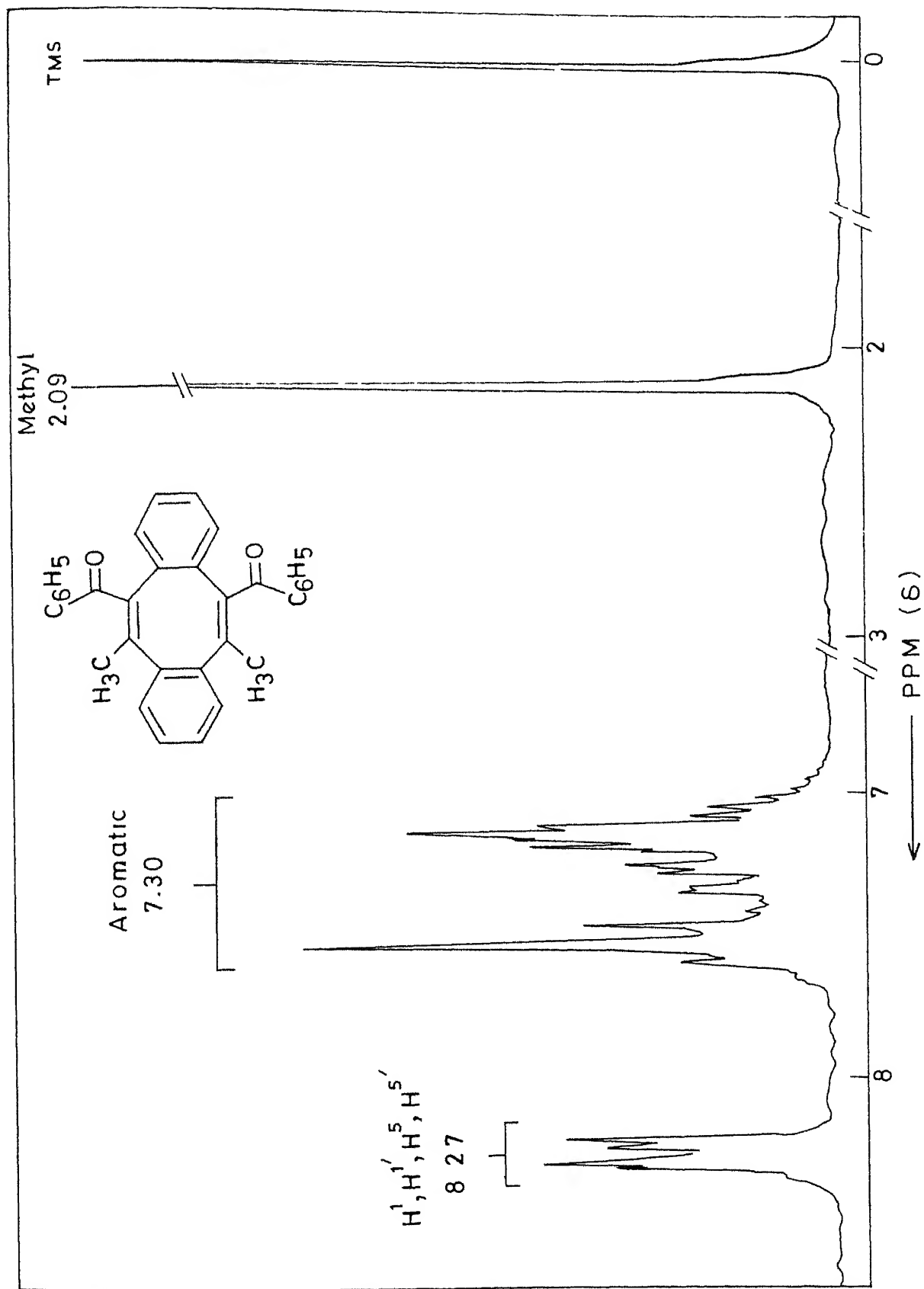


Fig II.19 ^1H NMR spectrum (100 MHz) of 57

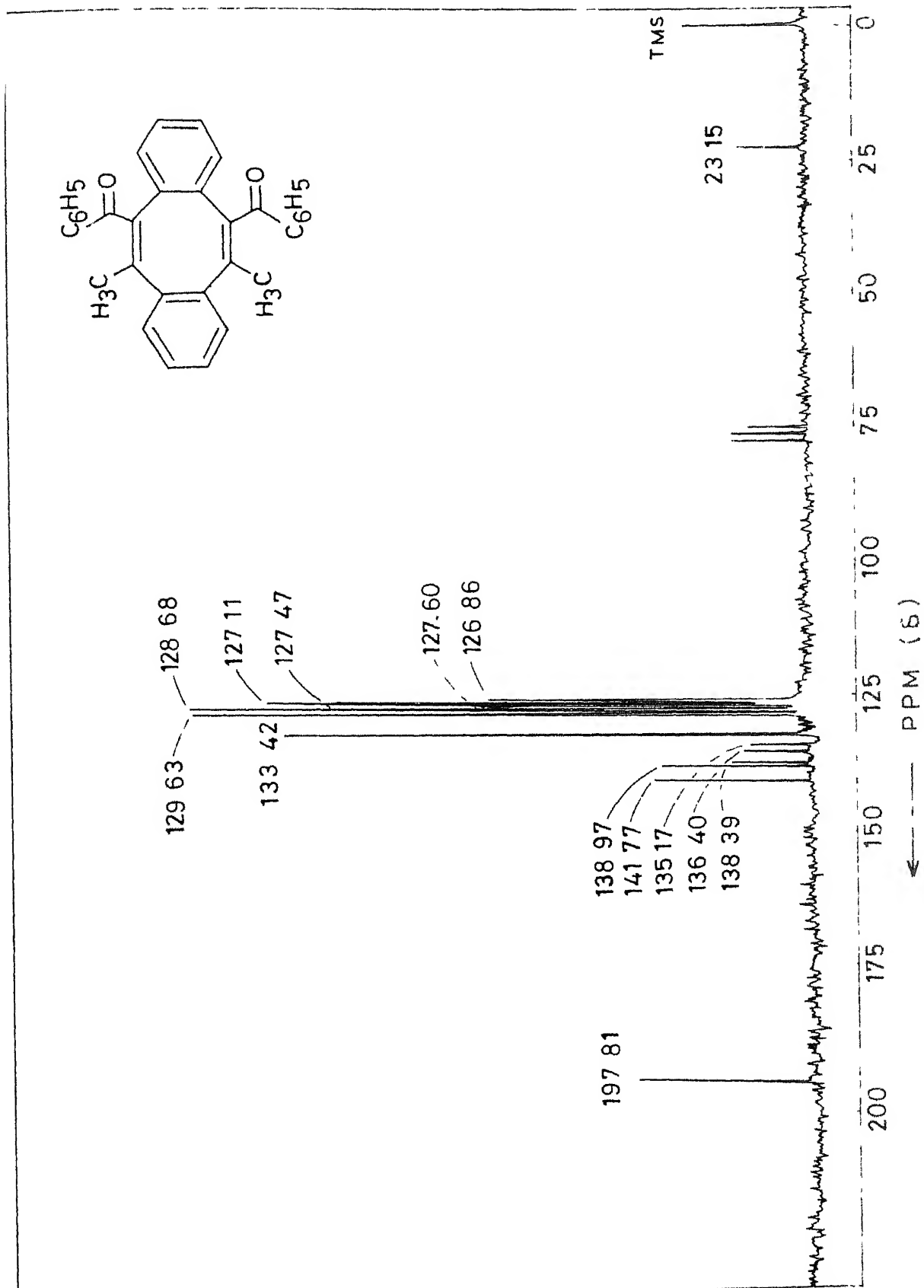


Fig II 20 ¹³C NMR spectrum, (25.2 MHz, CDCl₃) at 57

The mass spectrum of 57 (Fig. II.21) showed a molecular ion peak at m/e 440 (11). In addition, the spectrum showed several peaks at m/e 335 (8), 319 (12), 230 (12), 228 (10), 226 (9), 215 (20), 111 (12), 109 (10), 105 (100), 97 (21), 95 (17), 85 (25), 83 (30), 81 (25), 77 (49), 71 (43), 69 (39), 67 (17), 57 (56) and 43 (31). Some of the probable fragmentation modes are shown in Scheme II.13. The initial loss of a benzoyl group from the molecular ion of 57, for example, could lead to the fragment 57b at m/e 335, which in turn can lose a methyl group and a hydrogen atom to give the fragment 57c at m/e 319. Further loss of a benzoyl group from 57b, on the other hand, could give rise to 57e at m/e 230, which in turn could lose a methyl group to give 57d at m/e 215. The loss of two hydrogen atoms from 57e will, however, lead to 57f at m/e 228, which in turn can lose two more hydrogen atoms to give the fragment 57h at m/e 226.

If the structures 57 and 60 correctly represent some of the photoproducts derived from 37, then it would be reasonable to assume that the phototransformation of a dibenzocyclooctatetraene derivative such as 57 itself should give rise to 60. In support of this assumption, it has been observed that the irradiation of a methanol solution of 57 for 10 minutes resulted in a 20% yield of 60. It may also be mentioned in this connection that the photoisomerizations of cyclooctatetraene derivatives are known to give rise to products,

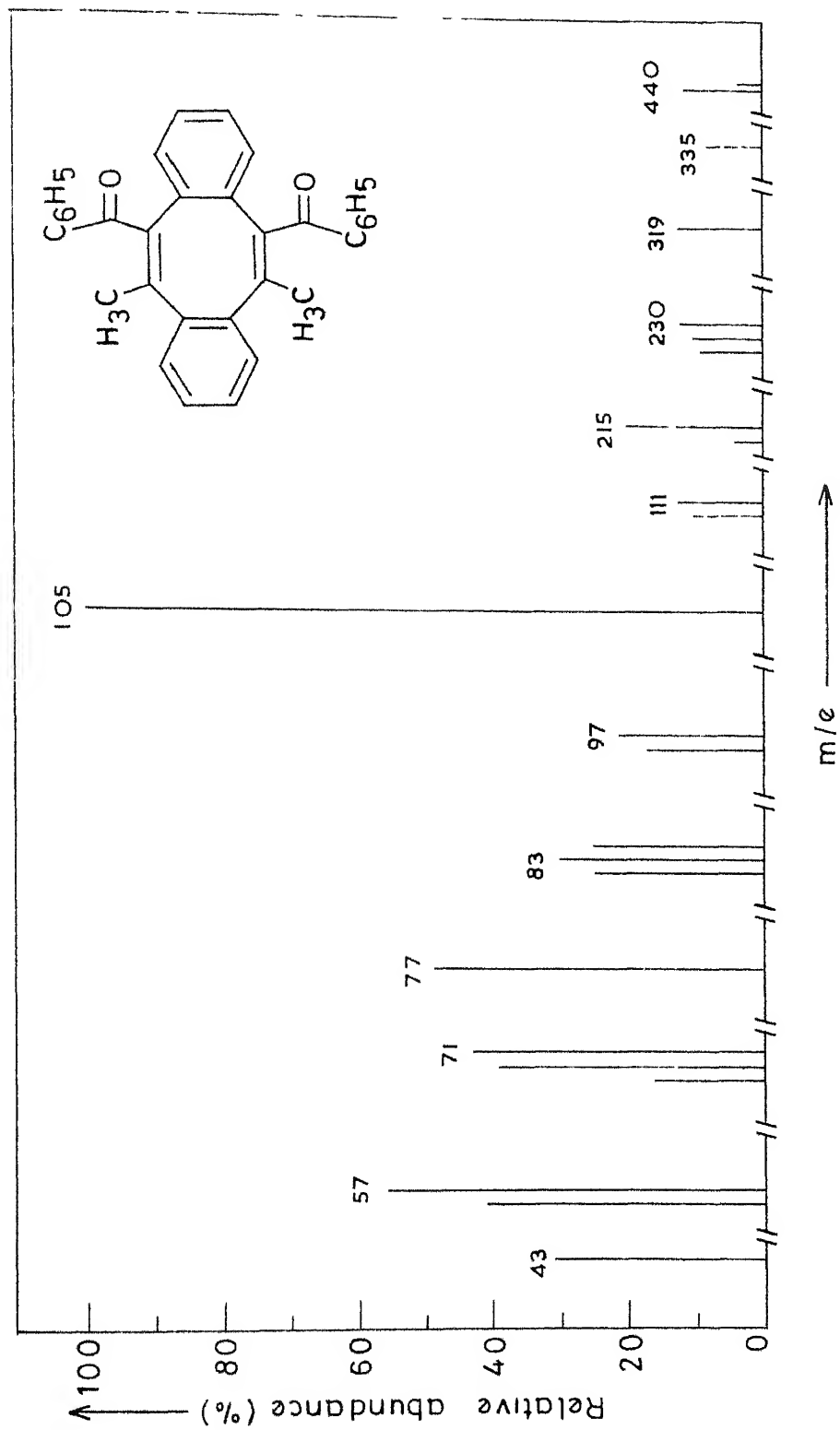
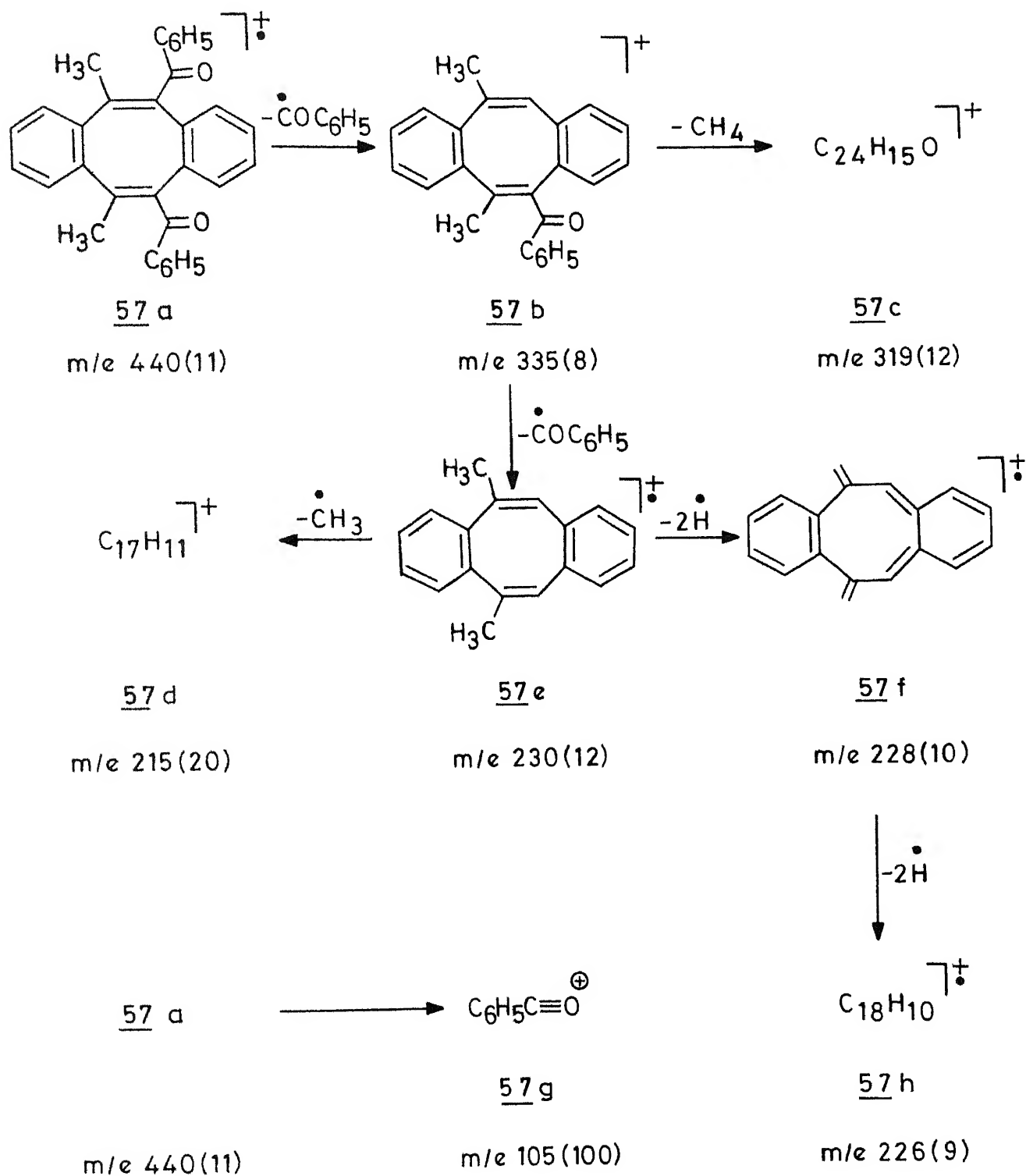


Fig. II. 21 Mass spectrum of 57.

Scheme II.13



The IR spectrum of the carbinol 63, for example, showed the presence of an OH band at 3530 cm^{-1} and did not show any carbonyl absorptions. The ^1H NMR spectrum of 63 (Fig. II.22) showed a sharp singlet at δ 1.21 (3 H), due to the methyl protons and a second singlet at δ 3.47 (1 H, D_2O -exchangeable) due to the hydroxyl proton. In addition, the spectrum showed two doublets at δ 4.64 (1 H, $J_{1',1''} = 13\text{ Hz}$) and 5.07 (1 H, $J_{1',1''} = 13\text{ Hz}$), due to the geminal protons of the exo-methylene group. The aromatic protons appeared as a complex multiplet, centred around δ 7.51 (18 H). The mass spectrum of 63 (Fig. II.23) showed a molecular ion peak at m/e 440 (56) and several other peaks at m/e 335 (58), 320 (29), 319 (41), 291 (12), 290 (15), 288 (25), 230 (29), 216 (47), 207 (50), 206 (25), 203 (13), 192 (28), 179 (51), 177 (18), 166 (30), 153 (19), 129 (21), 128 (17), 127 (23), 115 (53), 105 (100), 91 (29) and 77 (68).

The ^1H NMR spectrum of the indeno[1,2-a]indene derivative 65 (Fig. II.24), likewise showed several signals at δ 1.79 (3 H), 5.29 (s, 1 H), 5.64 (s, 1 H), 5.65 (s, 1 H), 7.28 (m, 16 H) and 8.19 (m, 2 H). Of these, the singlet at δ 1.79 has been assigned to the methyl group attached to the C-4b position, whereas the singlets at δ 5.29, 5.64 and 5.65 could be assigned to the exo-methylene protons at C-9 position and the methine proton at C-10 position. It may be mentioned in this connection that the geminal coupling between the

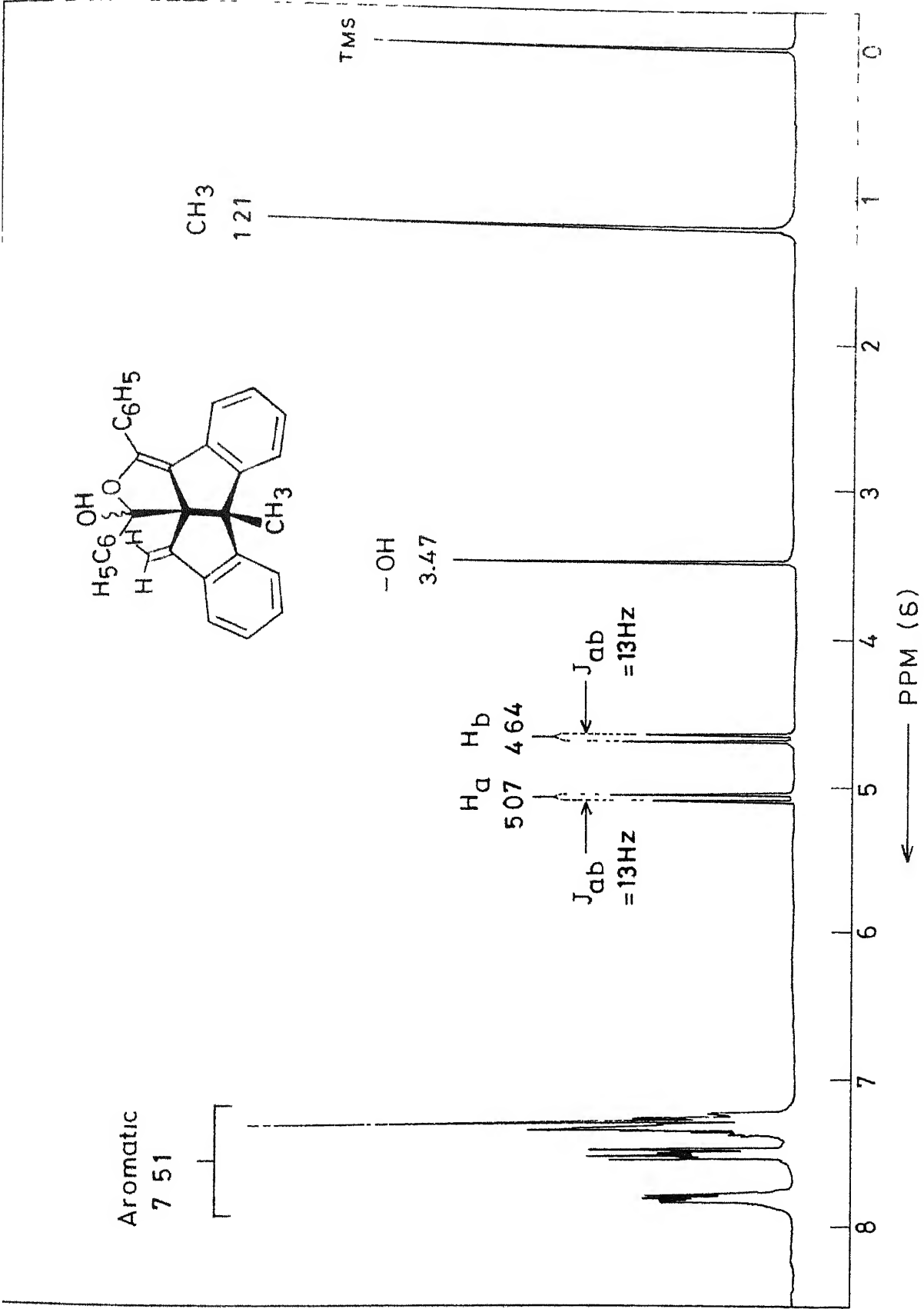


Fig II 22 ¹H NMR spectrum (270MHz) of 63

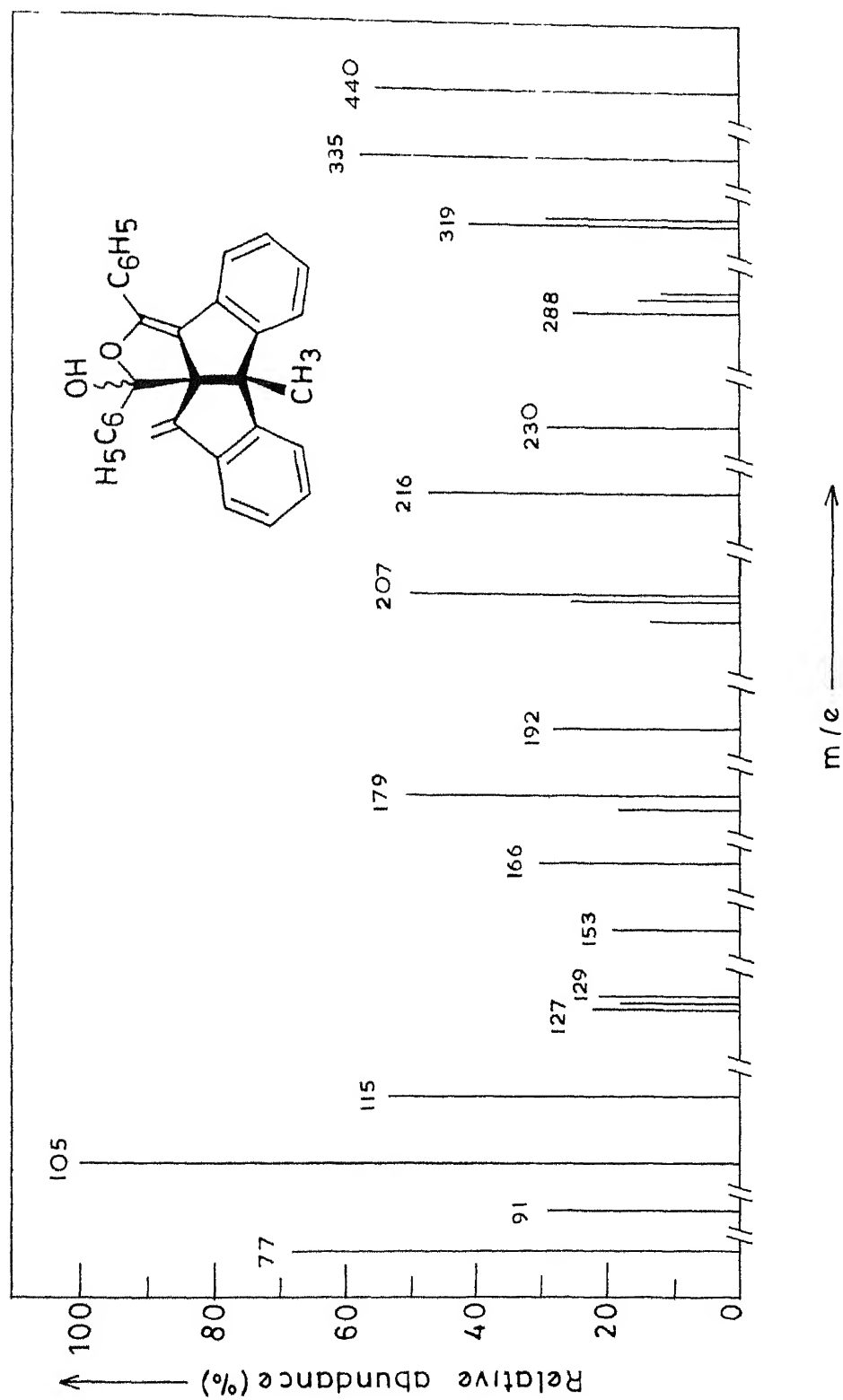


Fig. II. 23 Mass spectrum of 63.

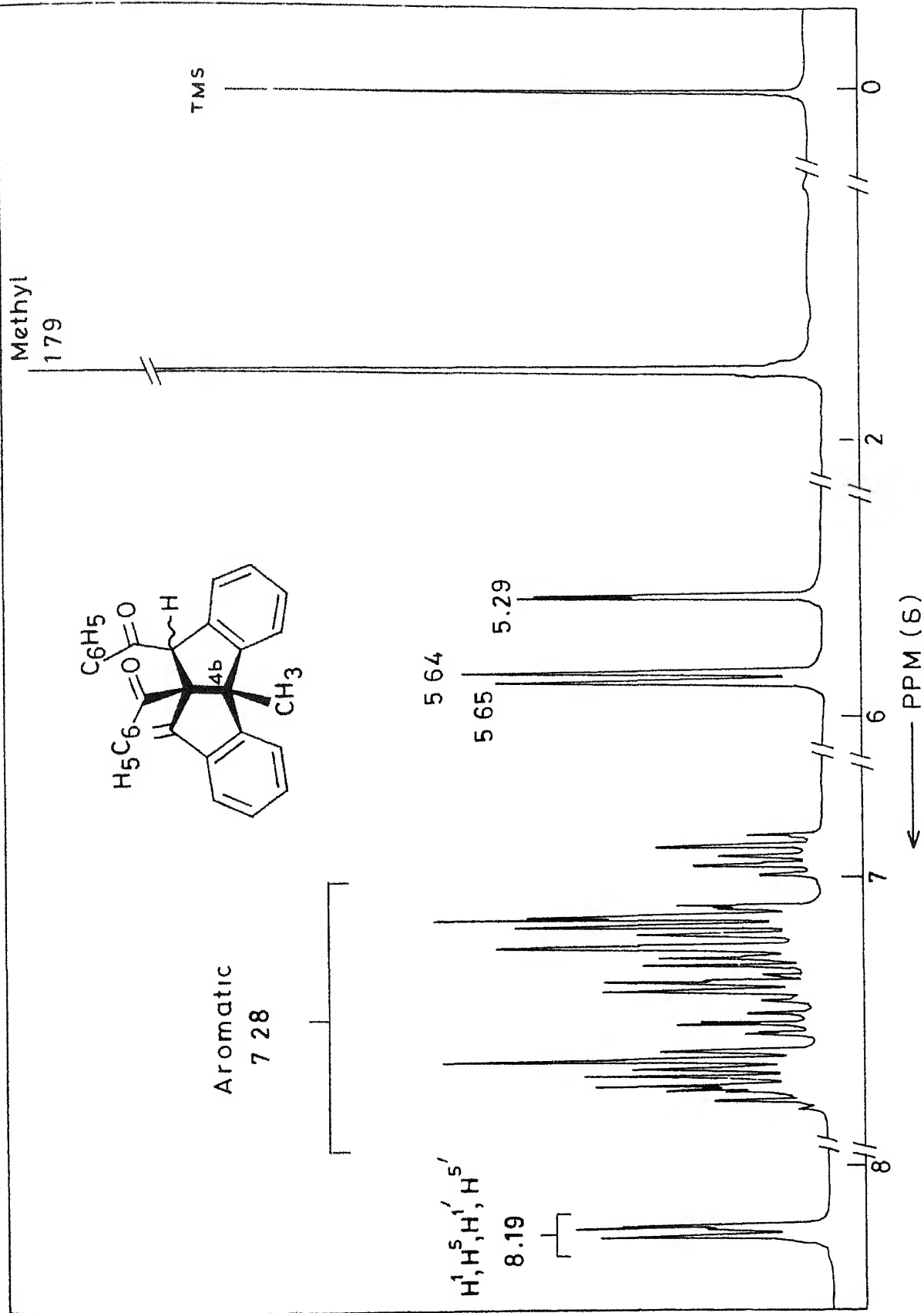


Fig II 24 ¹H NMR spectrum (270 MHz) of 65.

exo-methylene protons in 65 appears to be nearly zero and such cases are reported in the literature.⁵²

The ^{13}C NMR spectrum of 65 (Fig. II.25) showed several signals at δ 13.87, 23.48, 25.24, 78.64, 121.59, 123.80, 124.16, 125.07, 125.70, 127.9, 128.4, 132.20, 134.65, 136.5, 138.00, 138.4, 139.30, 148.85, 195.79 and 198.16. In addition, the spectrum showed several overlapping signals in the region, δ 128.40-130.4. The signals at δ 13.87, 23.48, 25.24 and 78.64 were assigned to the methyl carbon at C-4b, C-10, C-4b and C-9a carbons, respectively. The signal at δ 109.47 was assigned to exo-methylene carbon at C-9, whereas the signals at δ 195.79 and 198.16 have been assigned to the carbonyl carbons. The signals in the region δ 121.59-148.85 have been assigned to the remaining sp^2 carbons in 65.

The mass spectrum of 65 (Fig. II.26) showed a low intensity molecular ion peak at m/e 440 (7). Other peaks in the spectrum were observed at m/e 335 (28), 319 (6), 318 (17), 303 (6), 230 (6), 229 (2), 216 (6), 215 (34), 213 (10), 105 (100), 77 (20), 71 (9), 69 (10), 67 (5), 55 (14), 43 (18) and 41 (12). Some of the probable modes of fragmentation are shown in Scheme II.14. It would be reasonable to assume that the molecular ion of 65 will lose a benzoyl group to give the fragment 65b at m/e 335, which in turn can lose a second benzoyl group to give the fragment 65e, at m/e 230. The loss of a methyl group from 65e could lead to the fragment 65g

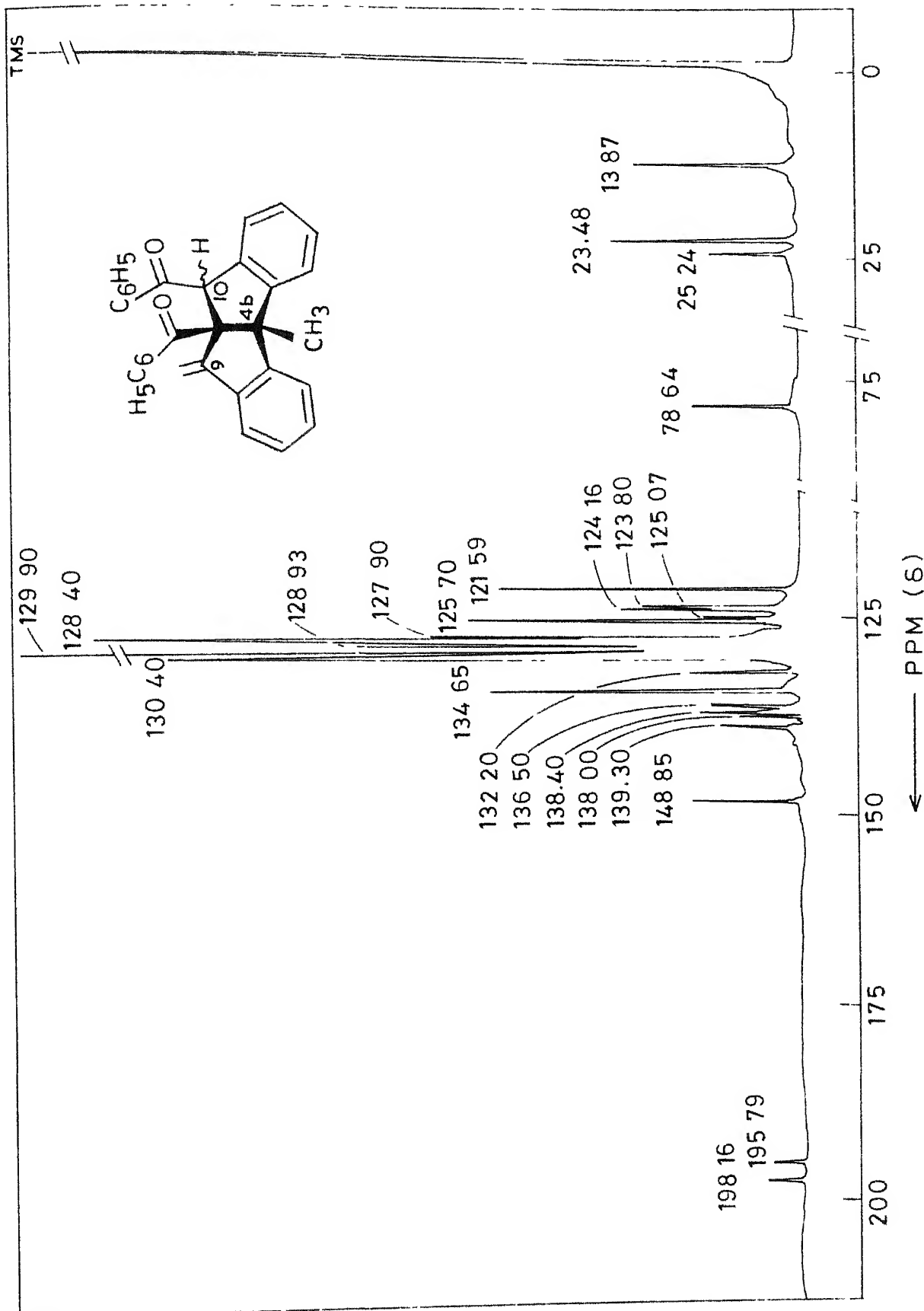


Fig II.25 ¹³C NMR spectrum (15.08 MHz) of 65.

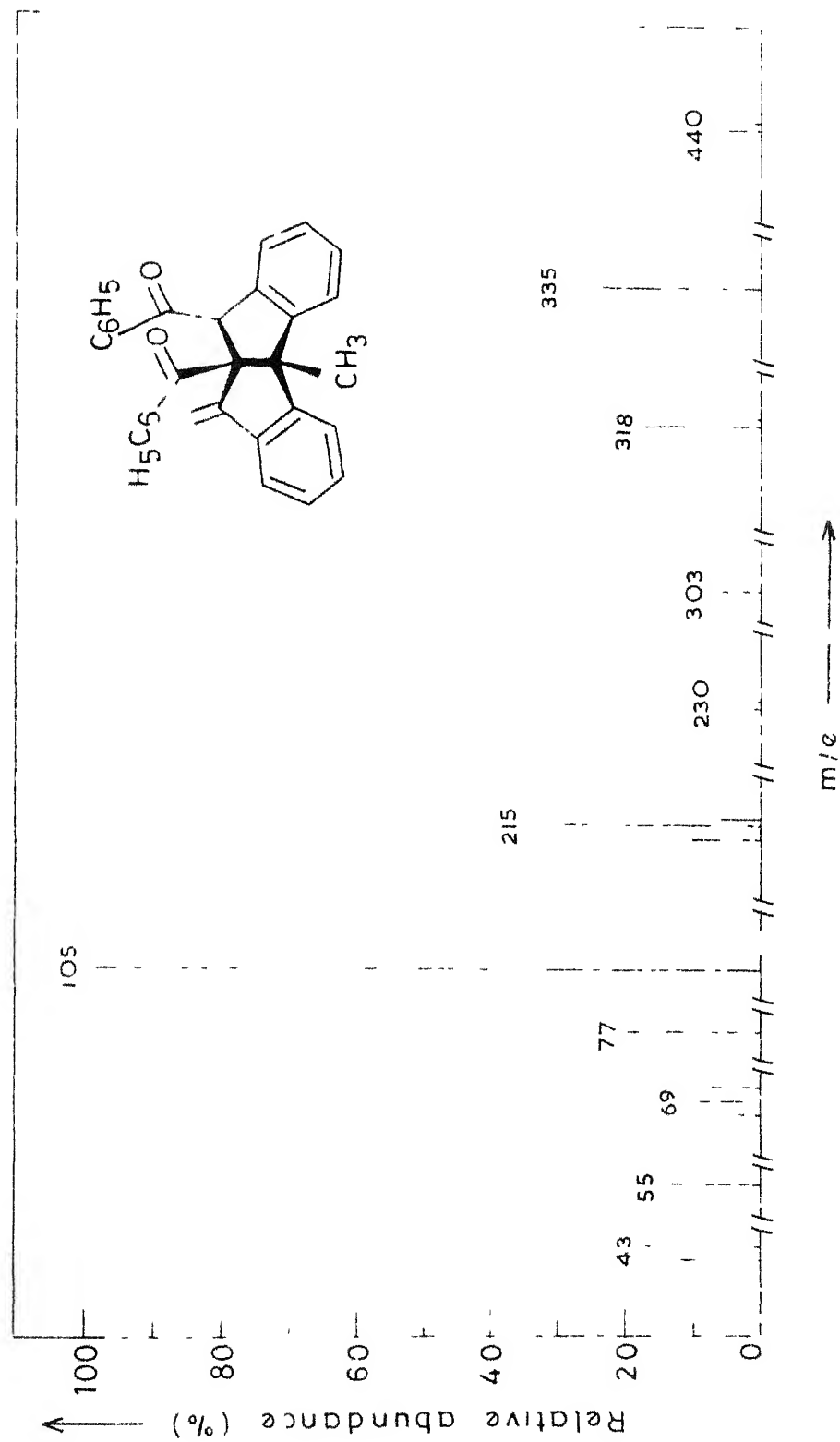
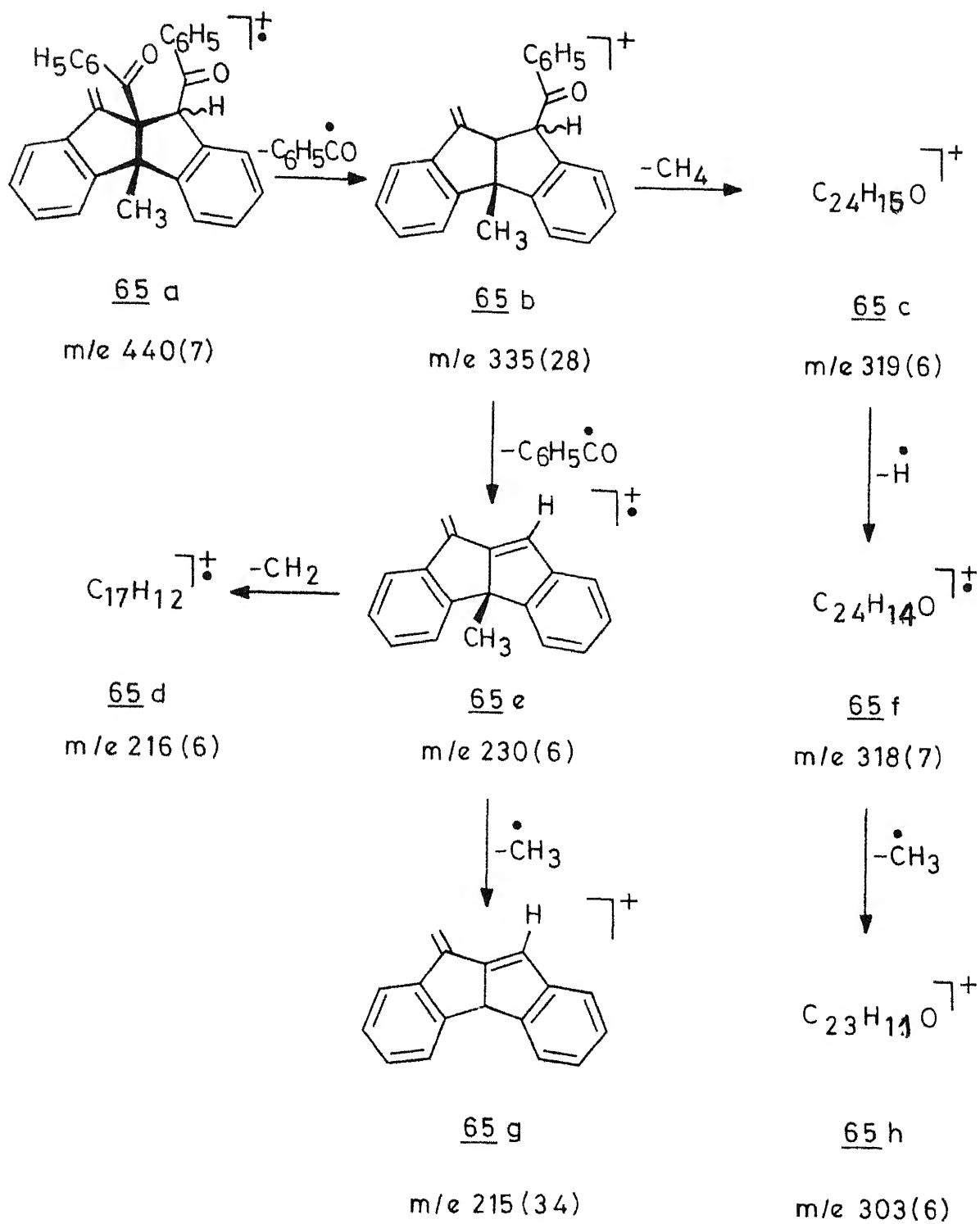


Fig II 26 Mass spectrum of 35

Scheme II.14

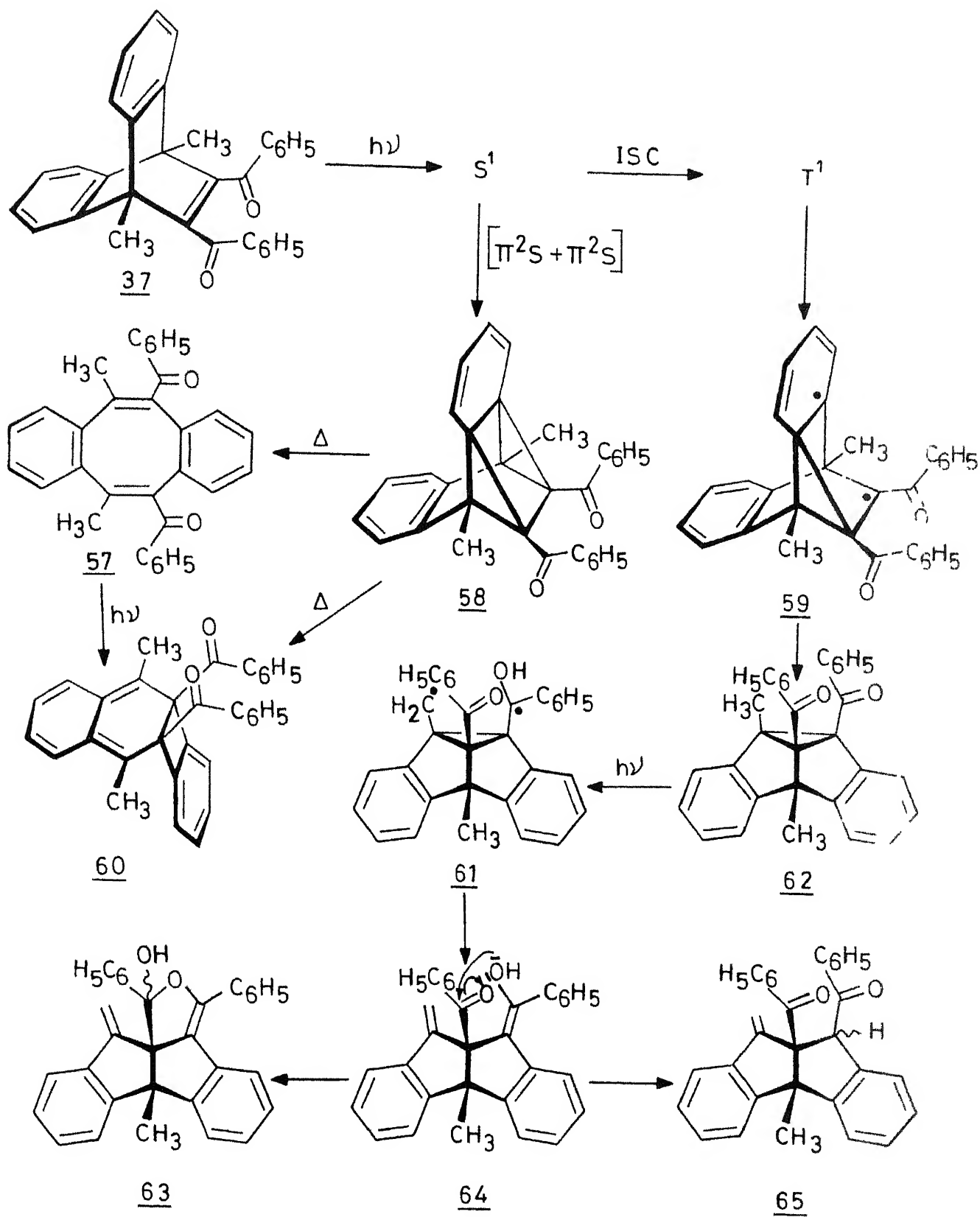


at m/e 215, whereas the loss of a methylene group from 65e will result in 65d at m/e 216. On the other hand, the loss of a methyl group and a hydrogen atom from the fragment ion 65b can lead to 65c at m/e 319, which in turn could lead to 65h, at m/e 303, through the loss of a hydrogen atom and one methyl group, via the cation 65f at m/e 318.

The formation of the different products such as 57, 60, 63 and 65 in the photoreaction of 35 could be rationalized in terms of the pathways shown in Scheme II.15. It would be reasonable to assume that the singlet excited state of 37 could bring about a [$\pi^2_s + \pi^2_s$] type of addition leading to the intermediate 58, which in turn can undergo thermal reversions to give 57 and 60. The cyclooctatetraene derivative 57 itself could give rise to 60, under photochemical conditions as has been shown in the present studies. It may be mentioned in this connection that tetraphenylcyclooctatetraene has been reported to give the corresponding bicyclo[4.2.0]octatriene derivative, under photochemical conditions.⁵¹

A second possible mode of reaction of 37 is the di- π -methane type of reaction, leading to the diradical intermediate 59, which can subsequently lead to the dibenzo-semibullvalene 62. It would be reasonable to assume that the semibullvalene 62, containing methyl and benzoyl groups attached to the cyclopropane ring, will undergo a Norrish type II

Scheme II 15



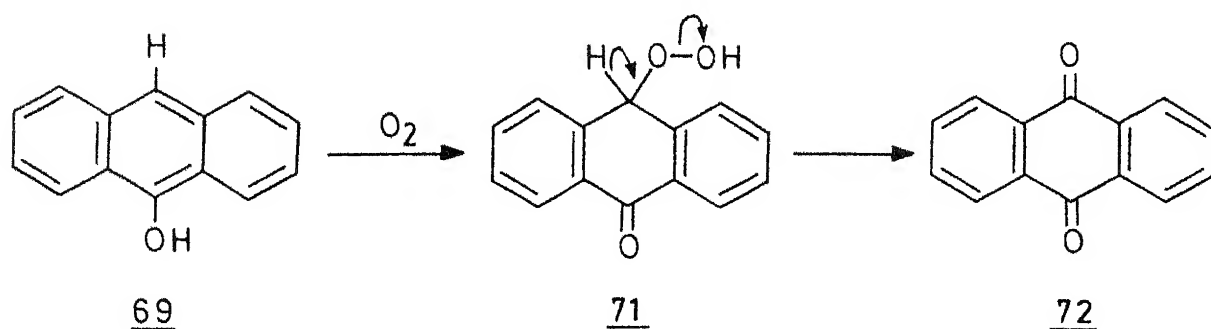
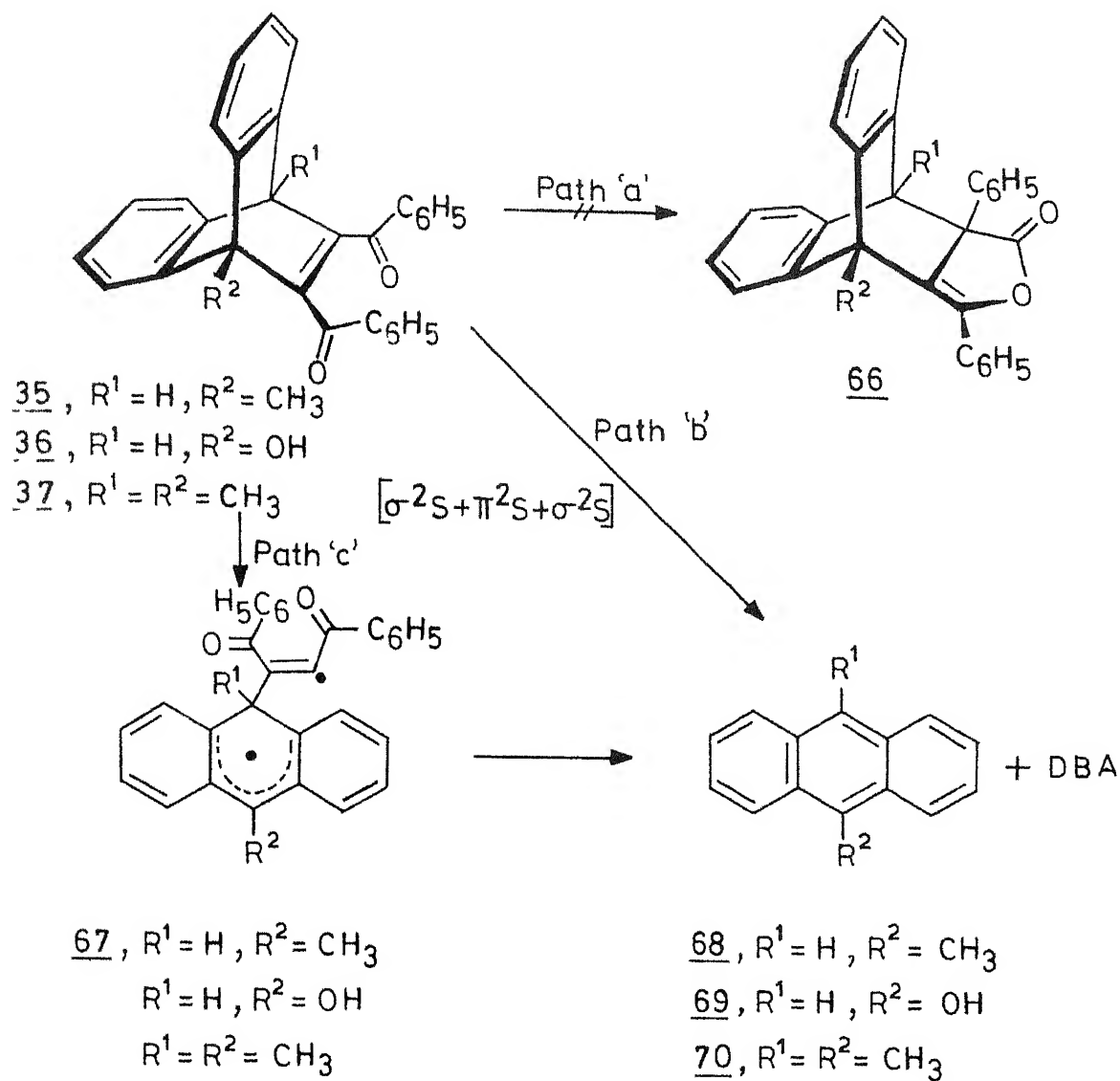
reaction, leading to the enol 64, presumably arising through the diradical intermediate 61. The enol 64 in turn can give rise to the carbinol 63 and the diketone 65, as shown in Scheme II.15.

II.3.3 Thermal Transformations of 11,12-Dibenzoyl-9,10-dihydro-9,10-ethenoanthracenes

It has been reported earlier⁴⁰ that the thermal transformations of a dibenzobarrelene derivative such as 34, containing a cis-1,2-dibenzoylalkene moiety as a part of its structural feature, involve a retro-Diels-Alder mode of fragmentation, leading to anthracene and not the heterohexatriene rearrangement to give 66 (Scheme II.16).

In the present studies, we have examined the thermal transformations of the dibenzobarrelene derivatives, 35, 36 and 37, containing different substituent groups at the bridgehead positions, with a view to understanding the preferred mode of reactions in these cases. Heating of 35 in refluxing diphenyl ether for 16 hr, for example, resulted in the isolation of a 23% yield of 9-methylanthracene (68), besides polymeric materials and a 27% recovery of the unchanged starting material (35). Similarly, thermolysis of 36, in refluxing diphenyl ether, for 8 hr gave a 26% yield of anthraquinone (72), besides polymeric materials. Heating of 37 around 300°, on the other hand, resulted in the formation of a 16% yield of

Scheme II 16



9,10-dimethylantracene (70), along with a small amount of benzoic acid (6%). In addition, 68% of the starting material (37) could also be recovered from this run.

The formation of products such as 9-methylantracene (68) and 9,10-dimethylantracene (70) in the thermolysis of 35 and 37, respectively, would suggest that in these cases also a retro-Diels-Alder type of fragmentation is taking place. It is however, unclear whether these reactions proceed by a concerted process (path 'b') or through a stepwise process (path 'c'), involving diradical intermediates such as 67 (Scheme II.16). The formation of anthraquinone (72), in the thermal reaction of 36, however, can be rationalized in terms of its initial fragmentation to the anthranol (69), which in turn can combine with oxygen of air to give the hydroperoxide intermediate 71. Loss of elements of water from the hydroperoxide 71 would give rise to anthraquinone (72), as shown in Scheme II.16.

II.4 EXPERIMENTAL

All melting points are uncorrected and were determined on a Mel-Temp melting-point apparatus. The IR spectra were recorded on Perkin-Elmer Model 377 or Model 580 infrared spectrophotometers. The electronic spectra were recorded on Beckman DB or Cary 17D spectrophotometers. NMR traces were recorded on Varian XL-100 and Bruker WH 270 NMR spectrometers,

using tetramethylsilane as internal standard. The mass spectra were recorded on a Varian Mat CH7 mass spectrometer at 70 eV. All the irradiation experiments were carried out either in a Srinivasan-Griffin Rayonet photochemical reactor (3500 Å) or by using a Hanovia 450-W medium-pressure mercury lamp in a quartz-jacketed immersion well.

The VPC analyses were carried out using a glass capillary column (OV-101, 11M H1319A) and hydrogen as carrier gas, on a Packard gas chromatograph, model 427 III, employing a flame ionization detector. The analyses were carried out with temperature programming, from 100-260° (6° per minute). The irradiation experiments for these studies were carried out in a Merry-go-round, using a 340 nm lamp source and in pyrex reaction tubes.

II.4.1 Starting Materials

11,12-Dibenzoyl-9,10-dihydro-9,10-ethenoanthracene (34), mp 212-213° was prepared in a 88% yield by a reported procedure.⁴⁶ Dibenzoylacetylene,^{53,54,55} mp 110-111°, 9-methylantracene,⁵⁶ mp 81° and 9,10-dimethylantracene,⁵⁷ mp 182° were prepared by known procedures. Solvents such as benzene, methanol and acetone were purified and dried by standard procedures. Petroleum ether used was the fraction, bp 60-80°.

IR spectrum (KBr) ν_{\max} : 3450 cm^{-1} ($\nu_{\text{O-H}}$), 3060 and 3020 cm^{-1} ($\nu_{\text{C-H}}$), 1630 and 1590 cm^{-1} ($\nu_{\text{C=C}}$).

UV spectrum (methanol) λ_{\max} : 268 nm (ϵ , 5,760) and 300 (2,000, sh).

II.4.4 Preparation of 11,12-Dibenzoyl-9,10-dihydro-9,10-dimethyl-9,10-ethenoanthracene (37)

A mixture of DBA (2.34 g, 0.01 mol), 9,10-dimethyl-anthracene (2.06 g, 0.01 mol) and anhydrous aluminum chloride (1.33 g, 0.01 mol) in methylene chloride (10 ml) was stirred at room temperature for 1/2 hr. Work-up of the reaction mixture as in the previous cases gave 3.6 g (83%) of 37, mp 262° (lit.⁴⁵, mp 261-263°), after recrystallization from chloroform.

II.4.5 Irradiation of 11,12-Dibenzoyl-9,10-dihydro-9,10-ethenoanthracene (34) in Methanol

A solution of 11,12-dibenzoyl-9,10-dihydro-9,10-ethenoanthracene (34) (533 mg, 1.29 mmol) in methanol (470 ml) was irradiated for 1/2 hr, using a 450-W Hanovia medium-pressure mercury lamp, and this experiment was repeated a few times to irradiate, in all, 1.6 g (3.88 mmol) of 34. The photolysed mixtures were combined together and the solvent was removed under vacuum to give a solid residue. Treatment of this residue with a 2% solution of aqueous sodium bicarbonate (9 ml) and acidification of the bicarbonate-extract with dilute hydrochloric acid (5%) gave 40 mg (8%) of benzoic acid, mp 122°

(mixture melting point), after recrystallization from a mixture (1:9) of benzene and petroleum ether.

The residue that was left behind, after treatment with bicarbonate solution, was chromatographed over silica gel. Elution with a mixture (1:9) of benzene and petroleum ether gave 843 mg (52%) of 1,2-dibenzoyldibenzotricyclo[3.3.0.0^{2,8}]-octa-3,6-diene (42), mp 188° (mixture melting point).⁴⁰

Further elution of the column with a mixture (1:4) of benzene and petroleum ether gave 500 mg (32%) of the unchanged starting material (34), mp 212° (mixture melting point), after recrystallization from acetone.

II.4.6 Irradiation of 11,12-Dibenzoyl-9,10-dihydro-9,10-ethenoanthracene (34) in Methanol, Saturated with Oxygen

A solution of 34 (500 mg, 1.2 mmol) in methanol (500 ml) was irradiated for 1/2 hr, using a 450-W Hanovia medium-pressure mercury lamp and under constant oxygen bubbling. Removal of the solvent under vacuum and treatment of the resultant residue with dilute sodium bicarbonate solution (2%), followed by acidification of the bicarbonate-extract gave 32 mg (22%) of benzoic acid, mp 122° (mixture melting point), after recrystallization from a mixture (1:9) of benzene and petroleum ether.

The residue left behind after bicarbonate extraction was chromatographed over silica gel. Elution with a mixture (1:9) of benzene and petroleum ether gave 235 mg (47%) of 42, mp 188° (mixture melting point).⁴⁰

Further elution of the column with a mixture (1:4) of benzene and petroleum ether gave 104 mg (21%) of the unchanged starting material, (34), mp 212° (mixture melting point).

II.4.7 Irradiation of 11,12-Dibenzoyl-9,10-dihydro-9,10-ethenoanthracene (34) in Acetone

A solution of 34 (200 mg, 0.48 mmol) in acetone (250 ml) was irradiated for 1/2 hr, using a 450-W Hanovia, medium-pressure mercury lamp. Removal of the solvent under vacuum and work-up of the resultant product mixture, as in the earlier cases gave 178 mg (89%) of 42, mp 188° (mixture melting point).

II.4.8 Hydrogenation of 1,2-Dibenzoyldibenzo-tricyclo[3.3.0.0^{2,8}]octa-3,6-diene (42)

A mixture of 42 (412 mg, 1 mmol) and 5% palladium on charcoal (350 mg) in THF (20 ml) was hydrogenated at 10 psi for 2 hr. After filtering off the catalyst, the solvent was removed under vacuum to give a product, which was recrystallized from acetone to give 250 mg (60%) of 9a,10-dibenzoyl-4b,9,9a,10-tetrahydro-cis-indeno[1,2-a] indene (41), mp 228-229°.

Anal. Calcd for $C_{30}H_{22}O_2$: C, 86.95; H, 5.31. Found: C, 87.38; H, 4.88.

IR spectrum (KBr) ν_{\max} : 3060, 3020 and 2950 cm^{-1} ($\nu_{\text{C-H}}$), 1690 cm^{-1} ($\nu_{\text{C=O}}$), 1610 and 1590 cm^{-1} ($\nu_{\text{C=C}}$).

UV spectrum (methanol) λ_{\max} : 250 nm (ϵ , 27,600), 290 (2,900, sh).

II.4.9 Irradiation of 11,12-Dibenzoyl-9,10-dihydro-9-methyl-9,10-ethenoanthracene (35) in Benzene

A solution of 35 (1.8 g, 4.22 mmol) in benzene (2000 ml) was irradiated for 1/2 hr in three lots, using a 450-W Hanovia medium-pressure mercury lamp. Removal of the solvent under vacuum from the combined photolysates gave a residue, which was treated with a 2% solution of sodium bicarbonate. Acidification of the bicarbonate extract with dilute hydrochloric acid gave 65 mg (12%) of benzoic, mp 122° (mixture melting point), after recrystallization from a mixture (1:9) of benzene and petroleum ether.

The material that was left behind after bicarbonate extract was chromatographed over silica gel. Elution with a mixture (1:4) of benzene and petroleum ether gave 980 mg (54%) of 8c,8d-dibenzoyl-4b,8b,8c,8d-tetrahydro-4b-methyldibenzo[a,b]-cyclopropa[c,d]pentalene (47), mp 193°, after recrystallization from a mixture (9:1) of methanol and methylene chloride.

Anal. Calcd for $C_{31}H_{22}O_2$: C, 87.55; H, 5.16; Mol. wt., 426. Found: C, 87.42; H, 5.11; Mol. wt., 426 (Mass spectrometry).

IR spectrum (KBr) ν_{\max} : 3065 and 2925 cm^{-1} ($\nu_{\text{C-H}}$), 1685 and 1670 cm^{-1} ($\nu_{\text{C=O}}$), 1605 and 1585 cm^{-1} ($\nu_{\text{C=C}}$).

UV spectrum (methanol) λ_{\max} : 251 nm (ϵ , 28,300), 275 (7,800, sh) and 300 (1,400, sh).

II.4.10 Irradiation of 11,12-Dibenzoyl-9,10-dihydro-9-methyl-9,10-ethenoanthracene (35) in Methanol

A solution of 35 (1.8 g, 4.22 mmol) in methanol (1800 ml) was irradiated for 1/2 hr, in three lots. Solvent from the combined photolysates was removed under vacuum and the resultant product mixture was worked up as in the earlier case by treatment with sodium bicarbonate solution (2%) to give 40 mg (8%) of benzoic acid, mp 122° (mixture melting point).

The material that was left behind after bicarbonate extraction was chromatographed over silica gel. Elution with a mixture (1:4) of benzene and petroleum ether gave 900 mg (50%) of 47, mp 193° (mixture melting point), after recrystallization from acetone.

Further elution of the column with a mixture (3:7) of benzene and petroleum ether gave 340 mg (19%) of the unchanged starting material (35), mp 181° (mixture melting point).

II.4.11 Irradiation of 11,12-Dibenzoyl-9,10-dihydro-9-methyl-9,10-ethenoanthracene (35) in Acetone

A solution of 35 (500 mg, 1.2 mmol) in acetone (500 ml) was irradiated for 1/2 hr, using a 450-W Hanovia medium-pressure mercury lamp. Removal of the solvent under vacuum and work-up of the residual solid, as in the earlier case gave 12 mg (8%) of benzoic acid, mp 122° (mixture melting point), 320 mg (64%) of 47, mp 193° (mixture melting point) and 75 mg (15%) of the unchanged starting material (35), mp 181° (mixture melting point).

II.4.12 Hydrogenation of 8c,8d-dibenzoyl-4b,8b,8c,8d-tetrahydro-4b-methyldibenzo[a,b]cyclopropa-[c,d]pentalene (47)

To a solution of 47 (426 mg, 1 mmol) in THF (20 ml) was added 400 mg of 5% palladium on charcoal and the mixture was hydrogenated at 10 psi for 2 hr. After filtering off the catalyst, the solvent was removed under vacuum to give a product, which on subsequent purification through preparative thin layer chromatography gave 9a,10-dibenzoyl-4b,9,9a,10-tetrahydro-4b-methyl-cis-indeno[1,2-a]indene (50), mp 213°.

Anal. Calcd for $C_{31}H_{24}O_2$: C, 86.91; H, 5.60. Found: C, 86.50; H, 4.93.

IR spectrum (KBr) ν_{\max} : 3060, 3020, 2960 and 2920 cm^{-1} ($\nu_{\text{C-H}}$), 1680 cm^{-1} ($\nu_{\text{C=O}}$), 1600 and 1580 cm^{-1} ($\nu_{\text{C=C}}$).

UV spectrum (methanol) λ_{\max} : 245 nm (ϵ , 23,500) and 285 (3,100).

II.4.13 Irradiation of 11,12-Dibenzoyl-9,10-dihydro-9-hydroxy-9,10-ethenoanthracene (36) in Benzene

A solution of 36 (2.78 g, 6.5 mmol) in benzene (1300 ml) was irradiated for 1 hr, in eight lots, in a Srinivasan-Griffin Rayonet photochemical reactor, using a 3500 Å light source. Removal of the solvent under reduced pressure from the combined photolysates gave a residual solid, which was extracted with aqueous sodium bicarbonate (2%). Acidification of the bicarbonate-extract with dilute hydrochloric acid gave 31 mg (4%) of benzoic acid, mp 122° (mixture melting point).

The product mixture that was left behind after bicarbonate extraction was chromatographed over silica gel. Elution with a mixture (1:20) of benzene and petroleum ether gave 725 mg (26%) of 9a,10-dibenzoyl-4b,9,9a,10-tetrahydro-9-oxo-cis-indeno[1,2-a]indene (55), mp 209-210°, after recrystallization from acetone.

Anal. Calcd for $C_{30}H_{20}O_3$: C, 84.11; H, 4.67; Found: C, 84.62; H, 4.40.

IR spectrum (KBr) ν_{\max} : 3080, 3060, 3040 and 2980 cm^{-1} ($\nu_{\text{C-H}}$), 1715 and 1675 cm^{-1} ($\nu_{\text{C=O}}$), and 1595 cm^{-1} ($\nu_{\text{C=C}}$).

UV spectrum (methanol) λ_{\max} : 253 nm (ϵ , 45,800) and 300 (4,100).

Further elution of the column with a mixture (1:9) of benzene and petroleum ether gave 1.39 g (50%) of the unchanged starting material (36), mp 212-213^o (mixture melting point), after recrystallization from benzene.

II.4.14 Irradiation of 11,12-Dibenzoyl-9,10-dihydro-9-hydroxy-9,10-ethenoanthracene (36) in Acetone

A solution of 36 (620 mg, 1.45 mmol) in acetone (620 ml) was irradiated for 1 hr, in four lots, in a Srinivasan-Griffin Rayonet photochemical reactor (3500 Å). Removal of the solvent under reduced pressure from the combined photolysates gave a product mixture, which was worked up as in the earlier case to give 17 mg (7%) of benzoic acid, mp 122^o (mixture melting point), 380 mg (62%) of 55, mp 209-210^o (mixture melting point) and 125 mg (20%) of the unchanged starting material (36), mp 212-213^o (mixture melting point).

II.4.15 Irradiation of 11,12-Dibenzoyl-9,10-dihydro-9,10-dimethyl-9,10-ethenoanthracene (37) in Benzene

A solution of 37 (1.1 g, 2.5 mmol) in benzene was irradiated for 1/2 hr, in two equal lots, in a Srinivasan-Griffin Rayonet photochemical reactor (3500 Å). Removal of the solvent under vacuum from the combined photolysates gave a residual solid, which was recrystallized from methylene chloride to give 500 mg (45%) of an isomeric, hydroxy compound (63), mp 180-181^o.

Anal. Calcd for $C_{32}H_{24}O_2$: C, 87.27; H, 5.45; Mol. wt., 440. Found: C, 87.50; H, 5.17; Mol. wt., 440 (Mass spectrometry).

IR spectrum (KBr) ν_{\max} : 3530 cm^{-1} (ν_{O-H}), 3060, 3030, 3010, 2960 and 2920 cm^{-1} (ν_{C-H}), 1650 and 1600 cm^{-1} ($\nu_{C=C}$).

UV spectrum (methanol) λ_{\max} : 255 nm (ϵ , 24,600).

The mother liquor, after the removal of 63, was extracted with an aqueous solution of sodium bicarbonate (2%). Acidification of the bicarbonate-extract with dilute hydrochloric acid gave 20 mg (7%) of benzoic acid, mp 122° (mixture melting point).

The organic layer, after extraction with bicarbonate solution, was concentrated under vacuum and subsequently chromatographed over silica gel. Elution of the column with a mixture (1:19) of benzene and petroleum ether gave 130 mg (12%) of 2,3-dibenzoyl-2,3-dihydro-1,4-dimethyl-2-benzonaphthalene (60), mp 154-155°, after recrystallization from cyclohexane.

Anal. Calcd for $C_{32}H_{24}O_2$: C, 87.27; H, 5.45; Mol. wt., 440. Found: C, 87.6; H, 5.1; Mol. wt., 440 (Mass spectrometry).

IR spectrum (KBr) ν_{\max} : 3053, 2977 and 2927 cm^{-1} (ν_{C-H}), 1663 cm^{-1} ($\nu_{C=O}$), 1590 and 1570 cm^{-1} ($\nu_{C=C}$).

UV spectrum (methanol) λ_{\max} : 243 nm (ϵ , 29,000), 313 (18,000) and 335 (11,500, sh).

Further elution of the column with a mixture (3:7) of benzene and petroleum ether gave 300 mg (27%) of 1,4-dibenzoyl-5,8-dimethyl-2,6-dibenzocyclooctatetraene (57), mp 211-212°, after recrystallization from acetone

Anal Calcd for $C_{32}H_{24}O_2$: C, 87.27; H, 5.45; Mol. wt., 440. Found. C, 87.48; H, 5.38; Mol. wt., 440 (Mass spectrometry).

IR spectrum (KBr) ν_{\max} : 3060 and 2970 cm^{-1} ($\nu_{\text{C-H}}$), 1652 cm^{-1} ($\nu_{\text{C=O}}$), 1605 and 1585 cm^{-1} ($\nu_{\text{C=C}}$).

UV spectrum (methanol) λ_{\max} : 250 nm (ϵ , 3,600) and 282 (8,100, sh).

II.4.16 Irradiation of 11,12-Dibenzoyl-9,10-dihydro-9,10-dimethyl-9,10-ethenoanthracene (37) in Methanol

A solution of 37 (1.10 g, 2.5 mmol) in methanol (1000 ml) was irradiated for 1/4 hr in two lots, using a 450-W Hanovia medium-pressure lamp. Removal of the solvent under vacuum gave a residual solid, which was extracted with aqueous sodium bicarbonate solution (2%). Acidification of the bicarbonate extract gave 25 mg (8%) of benzoic acid, mp 122° (mixture melting point).

The material that was left behind, after extraction with sodium bicarbonate, was chromatographed over silica gel. Elution with a mixture (1:19) of benzene and petroleum ether

gave 275 mg (25%) of 2,3-dibenzoyl-2,3-dihydro-1,4-dimethyl-2-benzonaphthalene (60), mp 154-155^o, (mixture melting point), after recrystallization from cyclohexane.

Further elution of the column with a mixture (3:7) of benzene and petroleum ether gave 297 mg (27%) of 1,4-dibenzoyl-5,8-dimethyl-2,6-dibenzocyclooctatetraene (57), mp 210-211^o (mixture melting point), after recrystallization from acetone.

Subsequent elution of the column with a mixture (1:1) of benzene and petroleum ether gave 70 mg (17%) of the unchanged starting material (37), mp 261-262^o (mixture melting point).

II.4.17 Irradiation of 11,12-Dibenzoyl-9,10-dihydro-9,10-dimethyl-9,10-ethenoanthracene (37) in Acetone

A solution of 37 (200 mg, 0.4 mmol) in acetone (200 ml) was irradiated for 1/4 hr, in a Srinivasan-Griffin Rayonet photochemical reactor (3500 Å). Removal of the solvent under vacuum from the reaction mixture gave a residual solid, which was extracted with an aqueous solution of sodium bicarbonate. Acidification of the bicarbonate extract with dilute hydrochloric acid gave 14 mg (9%) of benzoic acid, mp 122^o (mixture melting point), after recrystallization from a mixture (1:9) of benzene and petroleum ether.

The material that was left behind after extraction with bicarbonate was recrystallized from ethyl acetate to give

162 mg (80%) of 9a,10-dibenzoyl-4b,9,9a,10-tetrahydro-4b-methyl-9-methylene-cis-indeno[1,2-a]indene (65), mp 245°.

Anal. Calcd for $C_{32}H_{24}O_2$: C, 87.27; H, 5.45; Mol. wt., 440. Found: C, 87.00; H, 5.20; Mol. wt., 440 (Mass spectrometry).

IR spectrum (KBr) ν_{\max} : 3055, 3010, 2965, 2915 and 2865 cm^{-1} ($\nu_{\text{C-H}}$), 1685 and 1655 cm^{-1} ($\nu_{\text{C=O}}$), 1595 and 1575 cm^{-1} ($\nu_{\text{C=C}}$).

UV spectrum (methanol) λ_{\max} : 232 nm (ϵ , 22,400), 250 (28,200), 269 (8,500, sh), 297 (2,700, sh) and 310 (2,100, sh).

II.4.18 Irradiation of 1,4-Dibenzoyl-5,8-dimethyl-2,6-dibenzocyclooctatetraene (57) in Methanol

A solution of 57 (110 mg, 0.25 mmol) in methanol (150 ml) was irradiated for 1/4 hr, using a 450-W Hanovia medium-pressure lamp. Removal of the solvent under vacuum gave a product mixture, which was chromatographed over silica gel. Elution with a mixture (1:19) of benzene and petroleum ether gave 22 mg (20%) of 2,3-dibenzoyl-2,3-dihydro-1,4-dimethyl-2-benzonaphthalene (60), mp 154° (mixture melting point), after recrystallization from cyclohexane.

Further elution of the column with a mixture (1:9) of benzene and petroleum ether gave 36 mg (33%) of the unchanged, starting material (57), mp 210-211° (mixture melting point).

II.4.19 Thermolysis of 11,12-Dibenzoyl-9,10-dihydro-9-methyl-9,10-ethenoanthracene (35)

A solution of 35 (400 mg, 0.9 mmol) in diphenyl ether (25 ml) was refluxed for 16 hr and subsequently the solvent was removed under reduced pressure. The residue thus obtained was chromatographed over silica gel and elution with petroleum ether gave 42 mg (22%) of 9-methylanthracene, mp 81° (mixture melting point).

Further elution of the column with a mixture (1:4) of benzene and petroleum ether gave 272 mg (67%) of the unchanged starting material (35), mp 181° (mixture melting point).

II.4.20 Thermolysis of 11,12-Dibenzoyl-9,10-dihydro-9-hydroxy-9,10-ethenoanthracene (36) in Diphenyl Ether

A solution of 36 (428 mg, 1 mmol) in diphenyl ether (25 ml) was refluxed for 8 hr. Removal of the solvent under vacuum gave a product mixture, which was chromatographed over silica gel. Elution of the column with a mixture (1:19) of benzene and petroleum ether gave 110 mg (26%) of anthraquinone (72), mp $283-284^{\circ}$ (mixture melting point).

II.4.21 Thermolysis of 11,12-Dibenzoyl-9,10-dihydro-9,10-dimethyl-9,10-ethenoanthracene (37)

A sample of 37 (400 mg, 0.8 mmol) was heated in a sealed tube around 300° for 24 hr. Removal of the sublimed material from the cooler parts of the tube gave 5 mg (6%) of benzoic acid, mp 122° (mixture melting point).

The reaction mixture left inside the tube was chromatographed over silica gel. Elution with petroleum ether gave 30 mg (16%) of 9,10-dimethylantracene (70), mp 182° (mixture melting point).

Further elution of the column with a mixture (1:1) of benzene and petroleum ether gave 270 mg (68%) of the unchanged starting material (37), mp 261-262° (mixture melting point).

II.5 REFERENCES

1. H. E. Zimmerman and G. L. Grunewald, J. Am. Chem. Soc., 88, 183 (1966).
2. H. E. Zimmerman, R. W. Binkley, R. S. Givens and M. A. Sherwin, J. Am. Chem. Soc., 89, 3932 (1967).
3. H. E. Zimmerman, R. W. Binkley, R. S. Givens, G. L. Grunewald and M. A. Sherwin, J. Am. Chem. Soc., 91, 3316 (1969).
4. For some recent reviews, see, a) S. S. Hixson, P. S. Mariano and H. E. Zimmerman, Chem. Rev., 73, 541 (1973); b) H. E. Zimmerman in, "Rearrangements in Ground and Excited States", vol.3; P. de Mayo, ed., Academic Press, New York, 1980, p.131.
5. R. W. Rabideau, J. B. Hamilton and L. Friedman, J. Am. Chem. Soc., 90, 4465 (1968).
6. H. E. Zimmerman, R. S. Givens and R. M. Pagni, J. Am. Chem. Soc., 90, 6096 (1968).
7. H. E. Zimmerman, R. J. Boettcher, N. E. Buehler, G. E. Keck and M. G. Steinmetz, J. Am. Chem. Soc., 98, 7680 (1976).
8. R. S. Givens and W. F. Dettle, Chem. Commun., 1164 (1969).
9. C. A. Gröb, Angew. Chem., 81, 543 (1969).
10. J. P. N. Brewer and H. Heaney, Chem. Commun., 811 (1967).
11. R. S. H. Liu, J. Am. Chem. Soc., 90, 215 (1968).
12. R. K. Murray, Jr., and H. Hart, Tetrahedron Lett., 4995 (1968).
13. H. Hart and R. K. Murray, Jr., and G. L. Appleyard, Tetrahedron Lett., 4785 (1969).
14. H. D. Becker and B. Ruge, Angew. Chem. Internat. Ed., 14, 761 (1975).
15. H. E. Zimmerman, R. S. Givens and R. M. Pagni, J. Am. Chem. Soc., 90, 4191 (1968).

16. H. E. Zimmerman, R. S. Givens and R. M. Pagni, J. Am. Chem. Soc., 90, 6096 (1968).
17. E. Grovenstein, Jr., T. C. Campbell and T. Shibata, J. Org. Chem., 34, 2418 (1969).
18. R. S. Givens and W. F. Dettle, Chem. Commun., 1066 (1969).
19. H. Hart and R. K. Murray, Jr., Tetrahedron Lett., 379 (1969).
20. J. Ipaktschi, Tetrahedron Lett., 215 (1969).
21. L. A. Paquette and R. H. Meisinger, Tetrahedron Lett., 1479 (1970).
22. R. S. Givens and W. F. Dettle, J. Am. Chem. Soc., 93, 3963 (1971).
23. R. S. Givens, W. F. Dettle, R. L. Coffin and R. G. Carlson, J. Am. Chem. Soc., 93, 3957 (1971).
24. C. O. Bender and S. S. Shugarman, Chem. Commun., 934 (1974).
25. C. O. Bender and D. W. Brooks, Can. J. Chem., 53, 1684 (1975).
26. C. O. Bender and E. H. King-Brown, Chem. Commun., 878 (1976).
27. C. O. Bender and J. Wilson, Helv. Chim. Acta., 59, 1469 (1976).
28. H. E. Zimmerman and C. O. Bender, J. Am. Chem. Soc., 91, 7516 (1969).
29. H. E. Zimmerman and C. O. Bender, J. Am. Chem. Soc., 92, 4366 (1970).
30. C. O. Bender, J. L. M. Elder, A. J. Herbest and L. E. Miller, Can. J. Chem., 50, 395 (1972).
31. C. O. Bender and H. D. Burgess, Can. J. Chem., 51, 3486 (1973).
32. H. E. Zimmerman and M. L. Virriot-Villaume, J. Am. Chem. Soc., 95, 1274 (1973).

33. M. Demuth, C. O. Bender, S. E. Braslavsky, H. Görner, U. Burger, W. Amrein and K. Schaffner, *Helv. Chim. Acta.*, 62, 847 (1979).
34. M. Demuth, W. Amrein, C. O. Bender, S. E. Braslavsky, U. Burger, M. V. George, D. Lemmer and K. Schaffner, under publication.
35. E. Ciganek, *J. Am. Chem. Soc.*, 88, 2882 (1966).
36. H. Hart and R. K. Murray, Jr, *J. Am. Chem. Soc.*, 91, 2183 (1969).
37. H. Hart and G. M. Love, *J. Am. Chem. Soc.*, 95, 4592 (1973).
38. K. E. Richards, R. W. Tillman and G. J. Wright, *Aust. J. Chem.*, 28, 1289 (1975).
39. R. G. Paddick, K. E. Richards and G. J. Wright, *Aust. J. Chem.*, 29, 1005 (1976).
40. S. Lahiri, Ph.D. Thesis, Indian Institute of Technology, Kanpur (1977).
41. H. E. Zimmerman and D. R. Amick, *J. Am. Chem. Soc.*, 95, 3977 (1973).
42. H. E. Zimmerman, D. R. Amick and H. Hemetsberger, *J. Am. Chem. Soc.*, 95, 4606 (1973).
43. M. Kuzuya, E. Mano, M. Ishikawa, T. Okuda and H. Hart, *Tetrahedron Lett.*, 1613 (1981).
44. A. Hassner, *J. Org. Chem.*, 33, 2684 (1968).
45. D. M. McKinnon and J. Y. Wong, *Can. J. Chem.*, 49, 3178 (1971).
46. C. F. Willcox and M. P. Stevens, *J. Am. Chem. Soc.*, 84, 1258 (1962).
47. F. W. Wehrli and T. Wirthlin, "Interpretation of Carbon-13 NMR Spectra", Heyden, London, 1976.
48. G. C. Levy and G. L. Nelson, "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists", Wiley-Interscience, New York, 1972.

49. For a detailed discussion, see, Chapter I of this thesis.
50. M. V. George, Ch. Vijaya Kumar and J. C. Scaiano, J. Phys. Chem., 83, 2452 (1979).
51. E. H. White and R. L. Stern, Tetrahedron Lett., 193 (1964).
52. J. D. Roberts, "Nuclear Magnetic Resonance Applications to Organic Chemistry", McGraw-Hill, New York, 1959.
53. R. E. Lutz, Org. Synthesis, Coll. Vol. 3, A. H. Blatt, ed., John Wiley and Sons, Inc., New York, 1955, p.248.
54. G. S. Hammond, P. Watt, C. D. Delber and N. J. Turro, J. Am. Chem. Soc., 86, 2532 (1964).
55. R. E. Lutz and W. R. Smithey, J. Org. Chem., 16, 51 (1951).
56. E. Campaigne and W. L. Archer, J. Am. Chem. Soc., 75, 989 (1953).
57. G. M. Badger, F. Goulden and F. L. Warren, J. Chem. Soc., 18 (1941).

CHAPTER III

PHOTOCHEMICAL AND THERMAL TRANSFORMATIONS OF 2H-1,2,4-BENZOTHIADIAZINE 1,1-DIOXIDES

III.1 ABSTRACT

The photochemical and thermal transformations of a few thiadiazine 1,1-dioxides such as, 2H-1,2,4-benzothiadiazine-2-phenyl 1,1-dioxide (32), 2H-1,2,4-benzothiadiazine-3-methyl-2-phenyl 1,1-dioxide (33), 2H-1,2,4-benzothiadiazine-3-methyl-2-(2'-methylphenyl) 1,1-dioxide (34), 2H-1,2,4-benzothiadiazine-3-methyl-2-(4'-methylphenyl) 1,1-dioxide (35) and 2H-1,2,4-benzothiadiazine-2-cyclohexyl-3-methyl 1,1-dioxide (36), have been examined in the present studies.

Irradiation of 2H-1,2,4-benzothiadiazine-2-phenyl 1,1-dioxide (32) in methanol, for example, gave a mixture of products consisting of N-(2'-aminobenzenesulfonyl)aniline (25, 72%) and N-(2'-formamidobenzenesulfonyl)aniline (39, 8%). On the other hand, irradiation of 32 in benzene, gave exclusively 39 in a 68% yield. In contrast, the irradiation of 2H-1,2,4-benzothiadiazine-3-methyl-2-phenyl 1,1-dioxide (33) in methanol for 2 hr, gave a 44% yield of 5H-dibenzo[b,g][1,4,6]-thiadiazocine-6-methyl 12,12-dioxide (43), whereas the irradiation in benzene for 2½ hr gave 25% yield of 43. Similarly, the irradiation of 2H-1,2,4-benzothiadiazine-3-methyl-2-(2'-methylphenyl) 1,1-dioxide (34) in methanol gave a 33% yield of 5H-dibenzo[b,g][1,4,6]thiadiazocine-4,6-dimethyl 12,12-dioxide (44). Under analogous conditions, the irradiation of 34 in benzene gave a 37% yield of 44. Irradiation of 2H-1,2,4-benzothiadiazine-3-methyl-2-(4'-methylphenyl) 1,1-dioxide (35) in methanol, gave the corresponding ring-expanded product, 5H-dibenzo[b,g][1,4,6]thiadiazocine-2,6-dimethyl 12,12-dioxide (45) in a 33% yield. The irradiation of 35 in benzene, however, gave a 46% yield of 45.

Thermolysis of 2H-1,2,4-benzothiadiazine-2-phenyl 1,1-dioxide (32) by refluxing in diphenyl ether (250°) for 10 hr resulted in the formation of a 87% yield of N-(2'-formamidobenzenesulfonyl)aniline (39). In contrast, the thermolysis of the benzothiadiazine 1,1-dioxides, 33, 34 and 35, under

analogous conditions did not give rise to any isolable products; the unchanged starting materials were recovered in each case.

On the other hand, the thermolysis of 2H-1,2,4-benzothiadiazine-2-cyclohexyl-3-methyl 1,1-dioxide (36) by refluxing in diphenyl ether for 2½ hr gave an 82% yield of a product, identified as 2-amino-2,3-dihydro-2-methyl-1,3-benzothiazole 1,1-dioxide (55).

Reasonable mechanisms have been suggested for the formation of different products, in the photochemical and thermal transformations of the different benzothiadiazine derivatives, 32-36, that we have examined.

III.2 INTRODUCTION

Heterohexa-1,3,5-trienes containing hetero atoms such as oxygen, nitrogen and sulfur can, in principle, undergo thermal electrocyclic reactions to give heterocyclohexa-1,3-dienes,¹ through a $[\pi^2_s + \pi^2_s + \pi^2_s]$ process or the $[\pi^4_a + \pi^2_a]$ type of addition to give heterobicyclo[3.1.0]hexenes.² The same heterobicyclo[3.1.0] systems would be predicted to be formed by the photocyclizations of the corresponding heterohexa-1,3,5-trienes through a $[\pi^4_a + \pi^2_s]$ or $[\pi^4_s + \pi^2_a]$ type of addition. In addition to the above cyclizations, monocyclic five-membered rings can be formed from heterohexa-1,3,5-trienes through either a pentadienyl anion mode of cyclization³ or an intramolecular nucleophilic addition involving hetero atoms such as nitrogen,

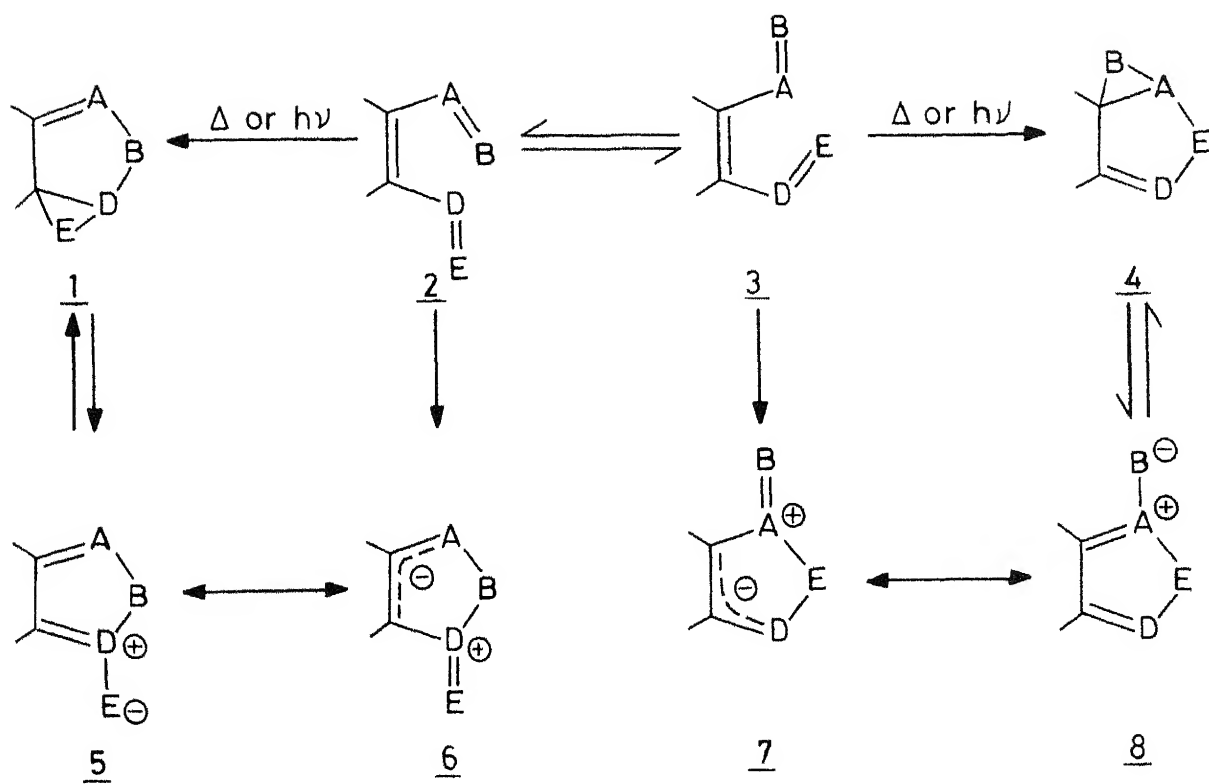
to the heterodiene part of the triene system.² Some of these possible modes of additions are shown in Scheme III.1.

Numerous examples of the thermal and photochemical transformations of heterohexa-1,3,5-trienes or their precursors such as the corresponding heterocyclohexa-1,3-dienes, are reported in the literature.² Gorewit and Rosenblum,⁴ for example, have shown that the sultones 9a,b are initially converted to the corresponding α,β -unsaturated sulfenes 10a,b, which in turn will lead to the dicarbonylalkenes 14a,b through the loss of sulfur monoxide. Further phototransformation of 14a,b would lead to the butenolides 12a,b, as shown in Scheme III.2.⁴

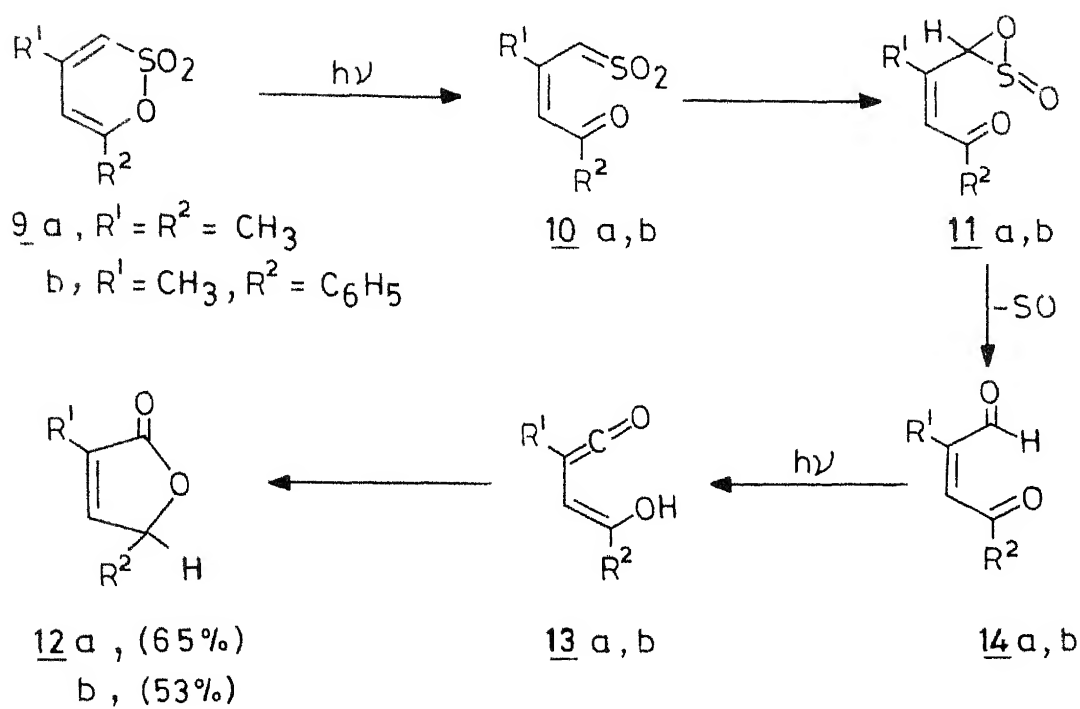
An analogous phototransformation is observed in the case of pulegone sultam (15), which is converted to the tetrahydroindole derivative 18, upon irradiation.⁵ It has been suggested that the initially formed heterohexa-1,3,5-triene 16, undergoes cyclization to give the dipolar intermediate 17, which can subsequently lose sulfur dioxide to give the tetrahydroindole derivative 18, as shown in Scheme III.3.

An interesting case of the thermal transformation of a benzoxadiazine system has been studied by Gilchrist et al.,⁶ who have shown that 3-*p*-tolyl-1,2,4-benzoxadiazine (19) is converted to 2-*p*-tolylbenzoxazole (23) in an 80% yield, on refluxing in chlorobenzene. The net loss of NH and the

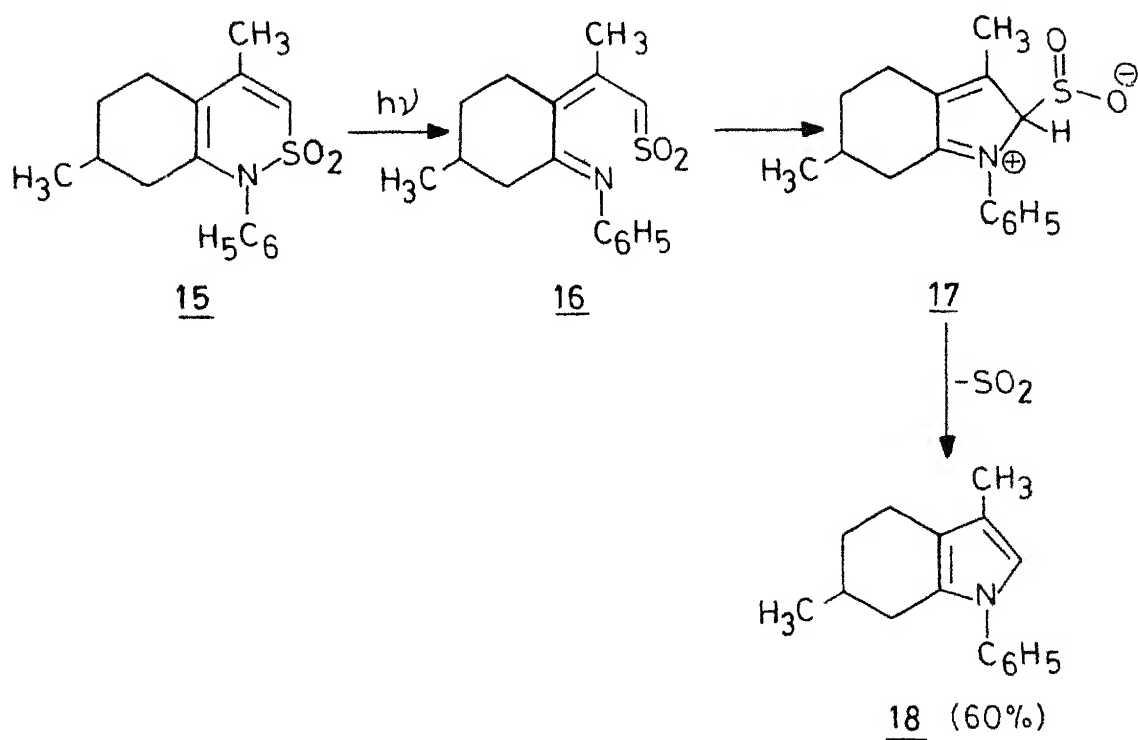
Scheme III.1



Scheme III 2



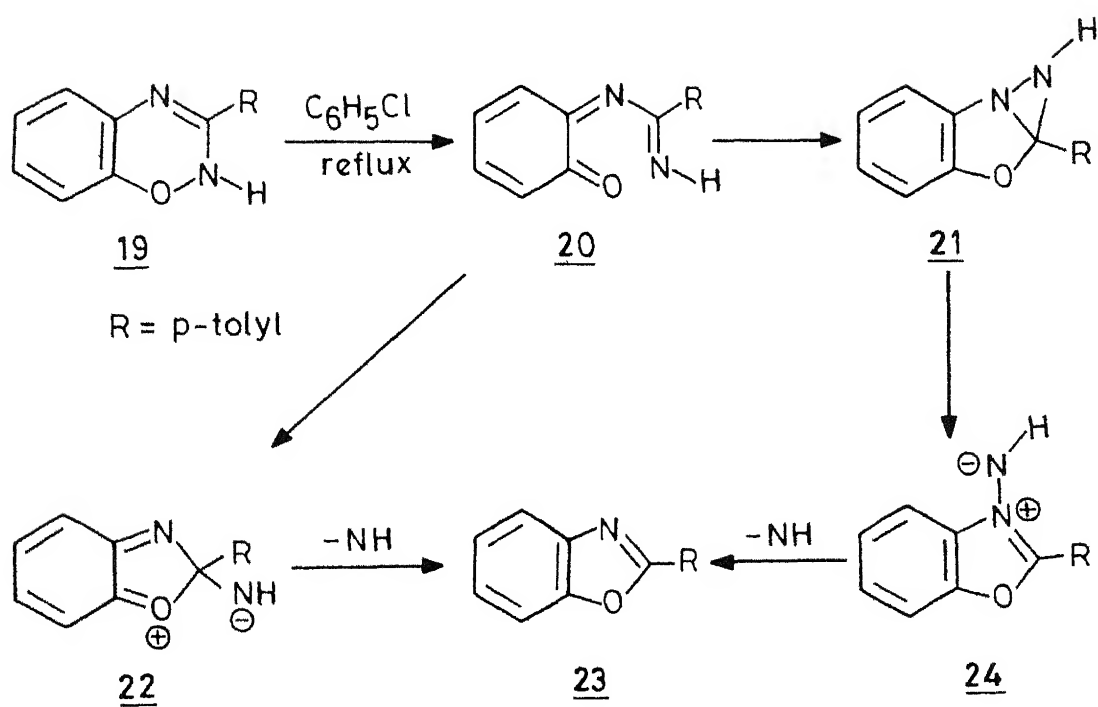
Scheme III 3



liberation of ammonia suggests the involvement of redox processes in these transformations. These authors have suggested that the initially formed heterohexa-1,3,5-triene 20, may be undergoing transformation to the benzoxazole 23, through the intermediates 21 and 24, as shown in Scheme III.4. The heterohexa-1,3,5-triene 20, can undergo transformation through an alternative pathway, involving the dipolar intermediate 22, leading to the product 23.

There have been no reports so far in the literature on either the thermal or photochemical transformations of benzothiadiazines, which could be viewed as precursors for heterohexa-1,3,5-triene systems, containing two nitrogen and one sulfur atoms. In this context, we have examined the photochemical and thermal transformations of a few 2H-1,2,4-benzothiadiazine 1,1-dioxides, with a view to examining the type of products formed in these transformations. Some of the benzothiadiazine 1,1-dioxides that we have examined include, 2H-1,2,4-Benzothiadiazine-2-phenyl 1,1-dioxide (32), 2H-1,2,4-benzothiadiazine-3-methyl-2-phenyl 1,1-dioxide (33), 2H-1,2,4-benzothiadiazine-3-methyl-2-(2'-methylphenyl) 1,1-dioxide (34), 2H-1,2,4-benzothiadiazine-3-methyl-2-(4'-methylphenyl) 1,1-dioxide (35) and 2H-1,2,4-benzothiadiazine-2-cyclohexyl-3-methyl 1,1-dioxide (36).

Scheme III.4



III.3 RESULTS AND DISCUSSION

III.3.1 Synthesis of 2H-1,2,4-Benzothiadiazine 1,1-Dioxides

Several reports have appeared in the literature concerning the synthesis of 2H-1,2,4-Benzothiadiazine 1,1-dioxides.⁷⁻¹² Freeman and Wagner,⁷ for example, had reported that the benzothiadiazine 1,1-dioxides such as 32 and 34 are formed in rather moderate yields, through the reaction of N-(2'-aminobenzenesulfonyl)aniline (25) and N-(2'-aminobenzenesulfonyl)-2-methylaniline (26), with the triethyl orthoesters 29 and 30, respectively. These workers had observed that iminoether intermediates 37 are formed in these reactions as by-products; however, their attempts to convert these iminoether intermediates to the corresponding benzothiadiazine 1,1-dioxides have not been successful.

In the present studies, we have observed that the benzothiadiazine 1,1-dioxides, 32-36 are conveniently prepared in good yields through the direct heating of the corresponding o-aminobenzenesulfonamide with the appropriate orthoester, around 130-140°, followed by heating of the reaction mixture at higher temperatures. Thus, heating of a mixture of N-(2'-aminobenzenesulfonyl)aniline (25) and triethyl orthoformate (29) around 130-140°, for ½ hr, followed by refluxing the mixture in diphenyl ether for an additional period of ½ hr gave a 75% yield of 2H-1,2,4-benzothiadiazine-2-phenyl 1,1-dioxide (32).

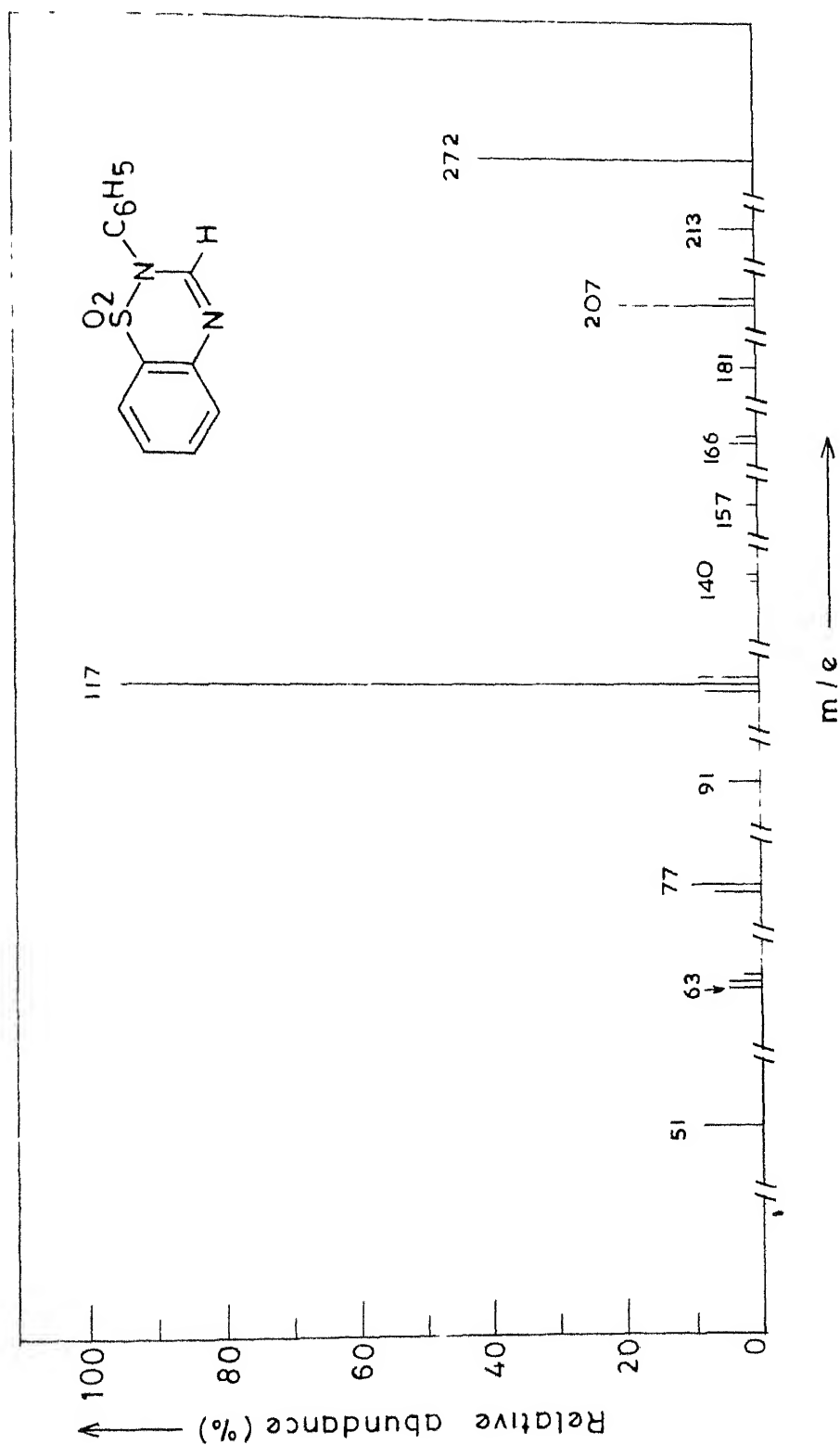
Similarly, heating of 25 with triethyl orthoacetate (30) around $130-140^{\circ}$, initially for $\frac{1}{2}$ hr, followed by refluxing of the mixture in diphenyl ether for $\frac{1}{2}$ hr, gave a 74% yield of 2H-1,2,4-benzothiadiazine-3-methyl-2-phenyl 1,1-dioxide (33).

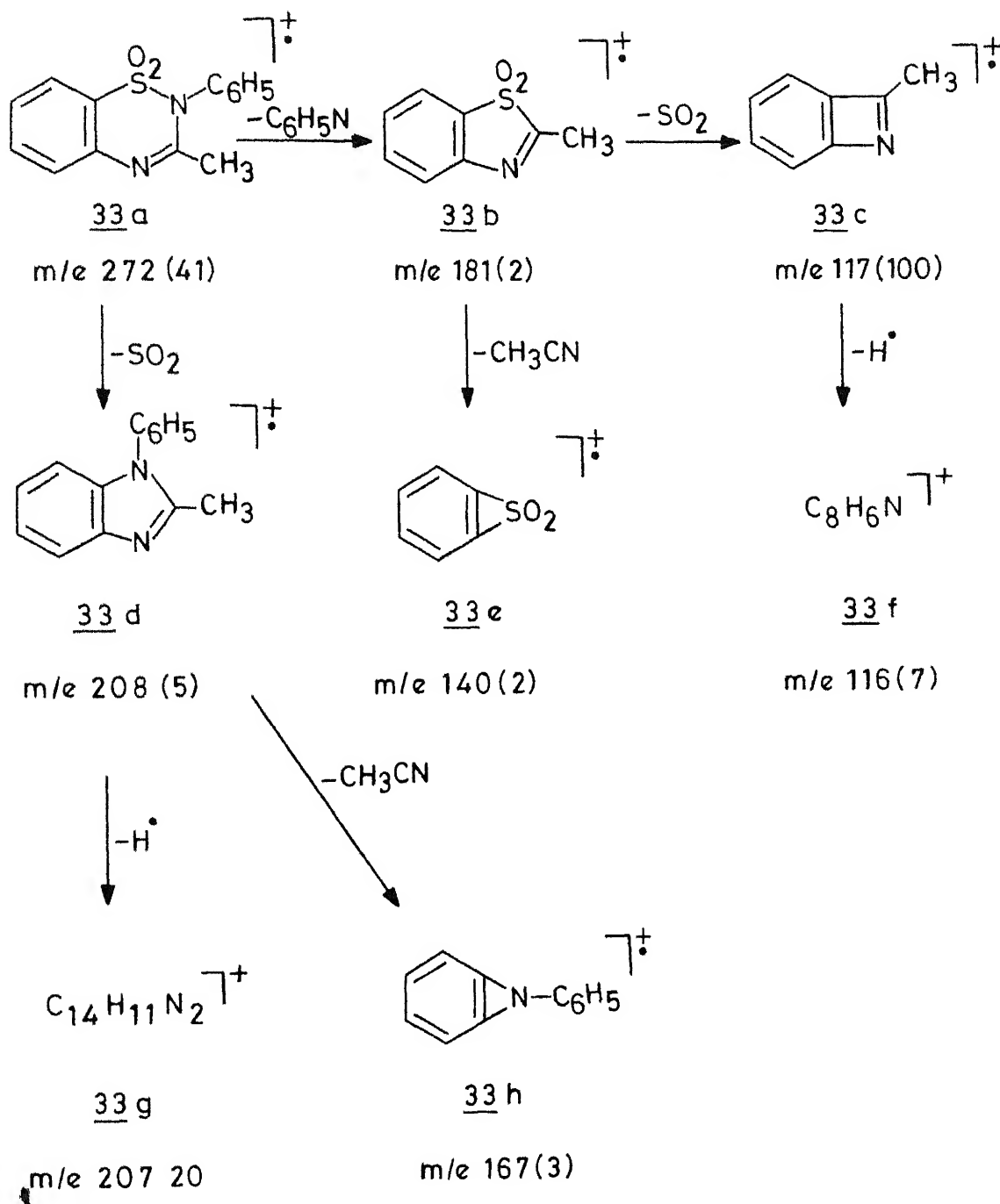
Likewise, the reaction of N-(2'-aminobenzenesulfonyl)-2-methylaniline (26) with triethyl orthoacetate (30), under conditions analogous to the formation of 32 and 33, gave a 65% yield of 2H-1,2,4-benzothiadiazine-3-methyl-2-(2'-methylphenyl) 1,1-dioxide (34), whereas, the reaction of N-(2'-aminobenzenesulfonyl)-4-methylaniline (27) with trimethyl orthoacetate (31), gave a 73% yield of 2H-1,2,4-benzothiadiazine-3-methyl-2-(4'-methylphenyl) 1,1-dioxide (35). Heating of a mixture of N-(2'-aminobenzenesulfonyl)cyclohexylamine (28) and trimethyl orthoacetate (31) for $\frac{1}{2}$ hr around 130° , on the other hand, gave a 74% yield of the iminoether derivative 37e. Refluxing of the iminoether derivative 37e in *o*-dichlorobenzene (198°) for 2 hr, however, gave a 69% yield of 2H-1,2,4-benzothiadiazine-2-cyclohexyl-3-methyl 1,1-dioxide (36).

The structures of the benzothiadiazine 1,1-dioxides, 32-36 have been arrived at on the basis of analytical data and spectral evidences (see, experimental section). With a view to understanding the modes of fragmentation of the benzothiadiazine 1,1-dioxides, under electron impact, we have examined the mass spectral fragmentations of a representative example such as 33.

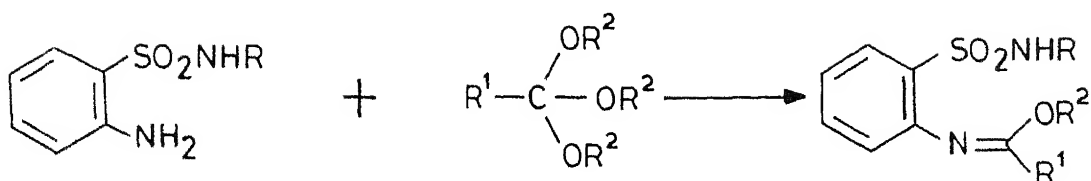
The mass spectrum of 33 (Fig. III.1) showed the molecular ion peak at m/e 272 (41). In addition, the spectrum showed several signals at m/e 213 (5), 208 (5), 207 (20), 181 (2), 167 (3), 166 (4), 157 (2), 140 (2), 139 (2), 118 (9), 117 (100), 116 (7), 91 (5), 77 (10), 76 (7), 65 (2), 64 (4), 63 (4) and 51 (9). Some of the probable modes of fragmentation of 33 are shown in Scheme III.5. The loss of a C_6H_5N fragment from the molecular ion can lead to 33b at m/e 181, which in turn can lose SO_2 to give the fragment 33c at m/e 117. Subsequent loss of a hydrogen atom from 33c can lead to 33f at m/e 116. The loss of an SO_2 fragment from the molecular ion, on the other hand, will result in 33d at m/e 208, which in turn can lose a hydrogen atom to give the fragment 33g at m/e 207. The loss of a CH_3CN fragment from 33d will, however, result in 33h at m/e 167.¹³

The formation of the 2H-1,2,4-benzothiadiazine 1,1-dioxides such as 32-36 in the reaction of the corresponding 2-aminobenzenesulfonamides with the appropriate orthoesters can be rationalised in terms of the pathway shown in Scheme III.6. It would be reasonable to assume that the o-aminobenzenesulfonamides 25-28 react with the appropriate orthoesters 29-31 to give initial intermediates 37a-e, which can subsequently lead to the benzothiadiazine 1,1-dioxides 32-36, at elevated temperatures, as shown in Scheme III.6.

Fig. III.1 Mass spectrum of 33

Scheme III.5

Scheme III 6



25 , R = C₆H₅

26 , R = C₆H₄-o-CH₃

27 , R = C₆H₄-p-CH₃

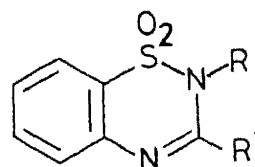
28 , R = C₆H₁₁

29 , R¹ = H, R² = C₂H₅

30 , R¹ = CH₃, R² = C₂H₅

31 , R¹ = R² = CH₃

37 a-e



32 , R = C₆H₅, R¹ = H

33 , R = C₆H₅, R¹ = CH₃

34 , R = C₆H₄-o-CH₃, R¹ = CH₃

35 , R = C₆H₄-p-CH₃, R¹ = CH₃

36 , R = C₆H₁₁, R¹ = CH₃

III.3.2 Photochemical Transformations of 2H-1,2,4-Benzothiadiazine 1,1-Dioxides

In the present studies, we have examined the photochemical transformations of a few benzothiadiazine 1,1-dioxides such as 2H-1,2,4-benzothiadiazine-2-phenyl 1,1-dioxide (32), 2H-1,2,4-benzothiadiazine-3-methyl-2-phenyl 1,1-dioxide (33), 2H-1,2,4-benzothiadiazine-3-methyl-2-(2'-methylphenyl) 1,1-dioxide (34) and 2H-1,2,4-benzothiadiazine-3-methyl-2-(4'-methylphenyl) 1,1-dioxide (35).

Irradiation of a solution of 32 in methanol for 1 hr, for example, gave a mixture of products consisting of N-(2'-aminobenzenesulfonyl)aniline (25, 72%) and N-(2'-formamido-benzenesulfonyl)aniline (39, 8%). On the other hand, the irradiation of 32 in benzene for 1½ hr, under analogous conditions, gave a 68% yield of 39. In addition, 10% of the starting material (32) could also be recovered from this run.

The structure of 39, was established on the basis of analytical data and spectral evidences. The ^1H NMR spectrum of 39, (Fig. III.2), for example, showed two singlets at δ 1.78 (1 H, D_2O -exchangeable) and δ 9.15 (1 H, D_2O -exchangeable), which could be assigned to the NH protons, whereas the complex multiplet centred around δ 7.83 (10 H) has been assigned to the aromatic protons and the formyl proton.

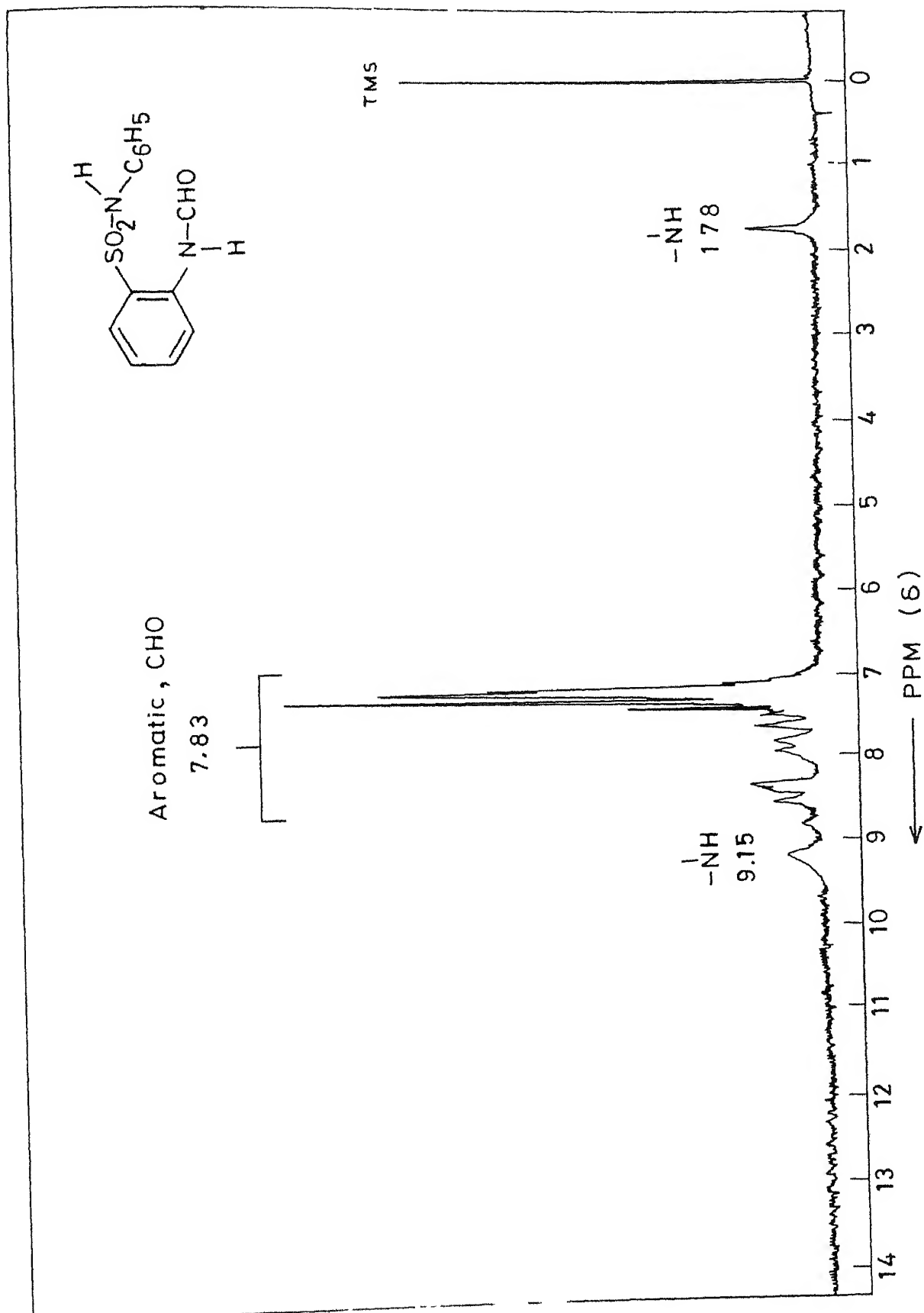


Fig. III 2 ^1H NMR spectrum (90 MHz) of 39

The mass spectrum of 39 (Fig. III.3) showed a molecular ion peak at m/e 276 (100). In addition, the spectrum showed several signals at m/e 259 (3), 258 (9), 248 (12), 196 (18), 184 (52), 183 (18), 182 (5), 167 (8), 166 (9), 156 (56), 140 (8), 122 (9), 120 (20), 108 (18), 92 (24) and 91 (17). Some of the probable fragmentation modes are shown in Scheme III.7.

Further proof of the structure of 39 was derived through its preparation in a 71% yield in the reaction of *N*-(2'-aminobenzenesulfonyl)aniline (25) with formic acid.

The formation of products such as 25 and 39 in the photoreaction of 32 may arise through the initial addition of elements of water to 32, under the reaction conditions, to give the carbinol 38, which in turn could lead to 39 (Scheme III.8). Further loss of carbon monoxide or a formyl group from 39, under photochemical conditions could result in the formation of 25. In support of this assumption, it has been observed that irradiation of 39 in methanol leads to a 71% yield of 25.

In contrast to the phototransformation of 32, irradiation of a solution of 2H-1,2,4-benzothiadiazine-3-methyl-2-phenyl 1,1-dioxide (33) in methanol gave a 40% yield of a product, identified as 5H-dibenzo[b,g][1,4,6]thiadiazocine-6-methyl 12,12-dioxide (43). Similarly, photolysis of 33 in benzene, however, gave a 25% yield of 43.

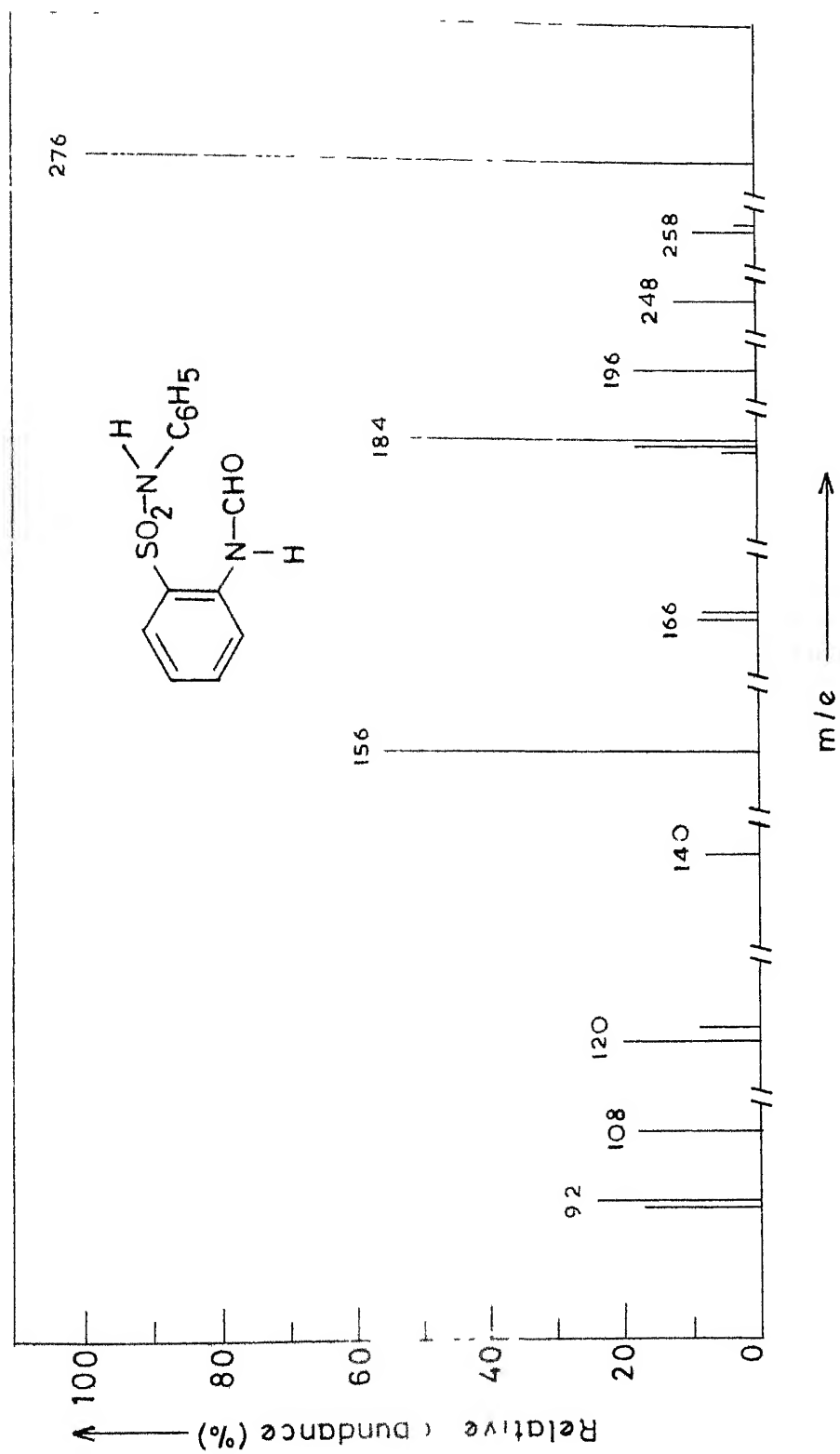
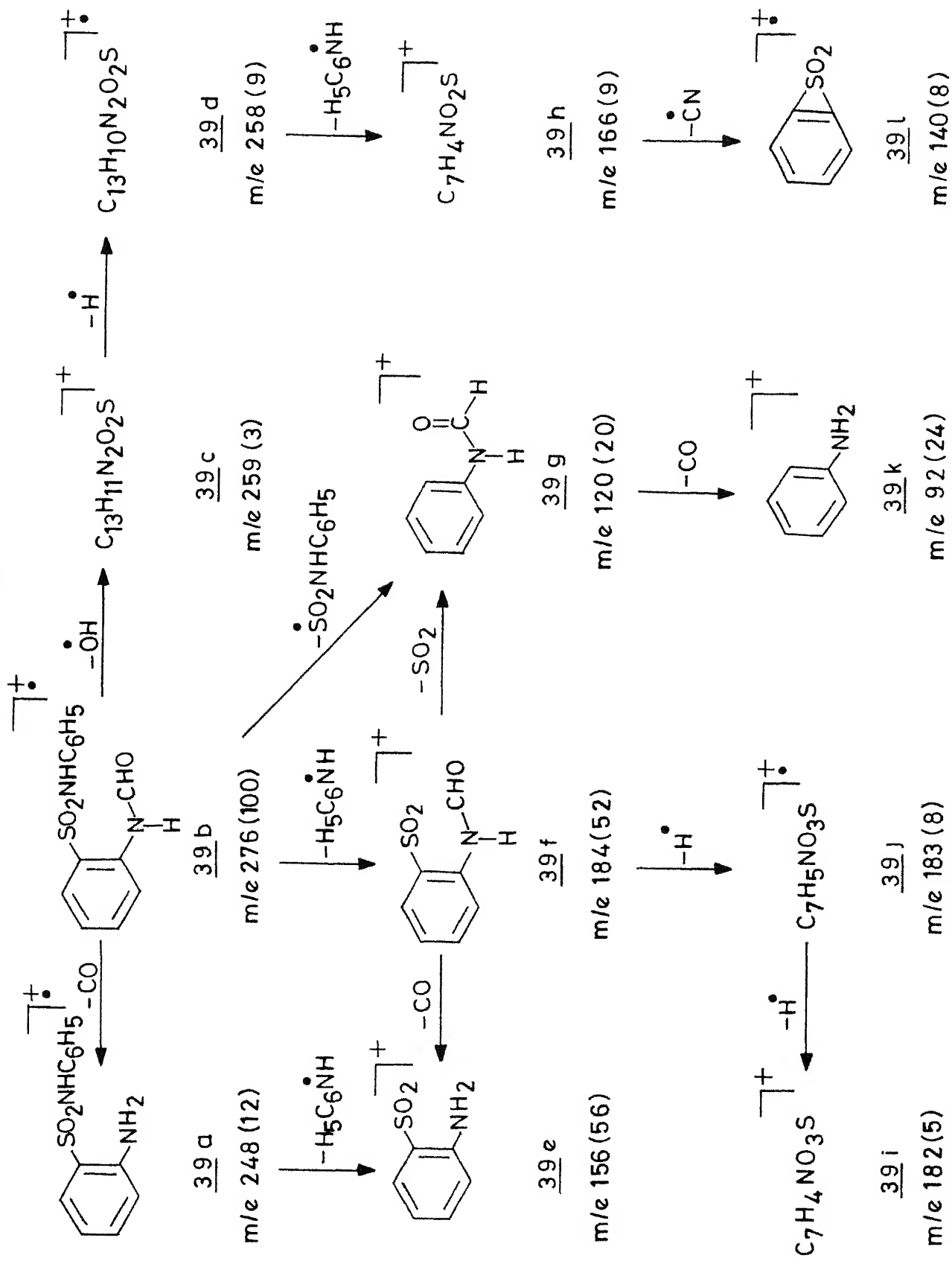


Fig. III 3 Mass spectrum of 39



The structure of 43 has been established on the basis of analytical data, spectral information and chemical evidence. The ^1H NMR spectrum of 43 (Fig. III.4), for example, showed a singlet at δ 2.36 (3 H), assigned to the methyl protons and a second singlet at δ 5.0 (1 H, D_2O -exchangeable), assigned to the NH proton. In addition, the spectrum showed a complex multiplet centred around δ 7.25 (6 H) due to the aromatic protons and a doublet of doublets centred around δ 7.78 (2 H), assigned to H-1 and H-11 protons ($J_{1,2} = J_{11,10} = 8$ Hz and $J_{1,3} = J_{11,9} = 2$ Hz). Down-field chemical shifts of H-1 and H-11 protons would be expected, owing to the proximity of the electron-withdrawing sulfone moiety. This is consistent with the observed chemical shifts for aromatic hydrogens, adjacent to a sulfonyl group.¹³

The mass spectrum of 43 (Fig. III.5) showed the molecular ion peak at m/e 272 (3). Other peaks in the spectrum were observed at m/e 209 (4), 207 (100), 167 (3), 166 (3), 140 (2), 139 (2), 131 (2), 104 (2), 103 (3), 91 (2), 90 (1), 77 (4) and 64 (2). Some of the probable fragmentation modes are shown in Scheme III.9. Loss of an SO_2H fragment from the molecular ion 43a can lead to 43b at m/e 207, which in turn can lose a C_6H_4 fragment to give 43e at m/e 131. Subsequent loss of a CH_3CN fragment¹⁵ from 43e will result in 43h at m/e 90. On the other hand, loss of a $\text{C}_8\text{H}_8\text{N}_2$ fragment from 43a will give rise to 43d at m/e 140, which can then lose a C_6H_4 fragment to give 43g at m/e 64.

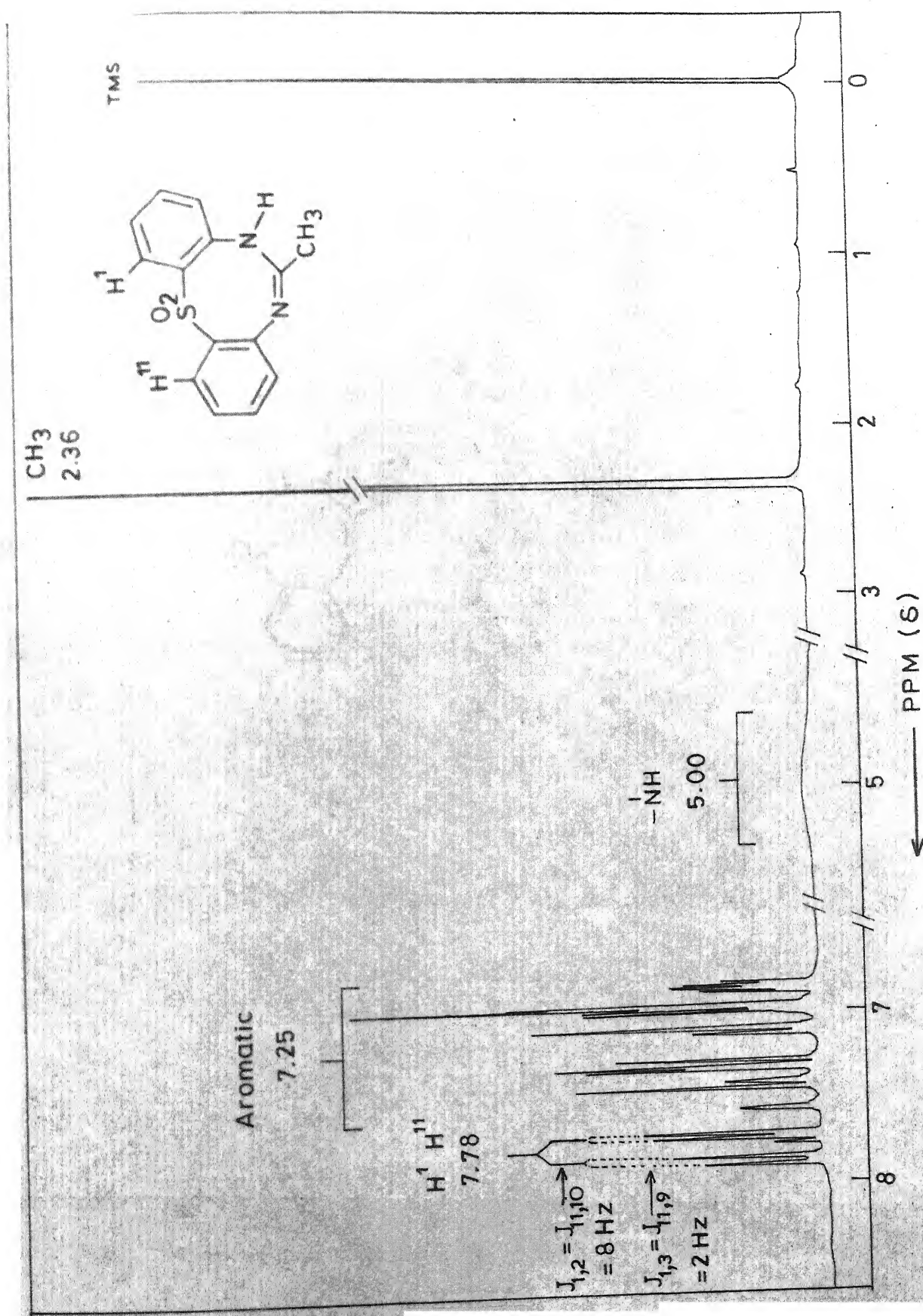
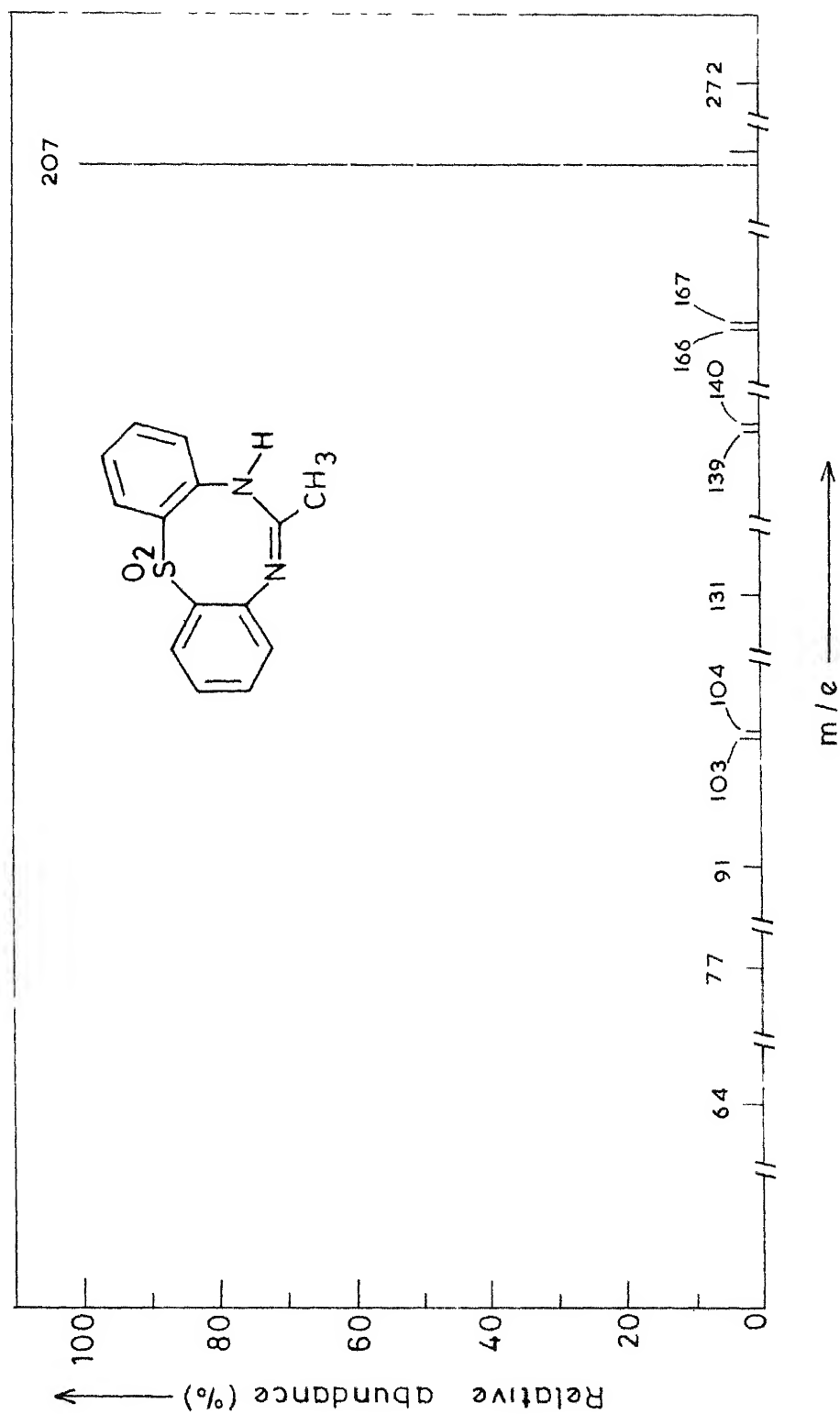
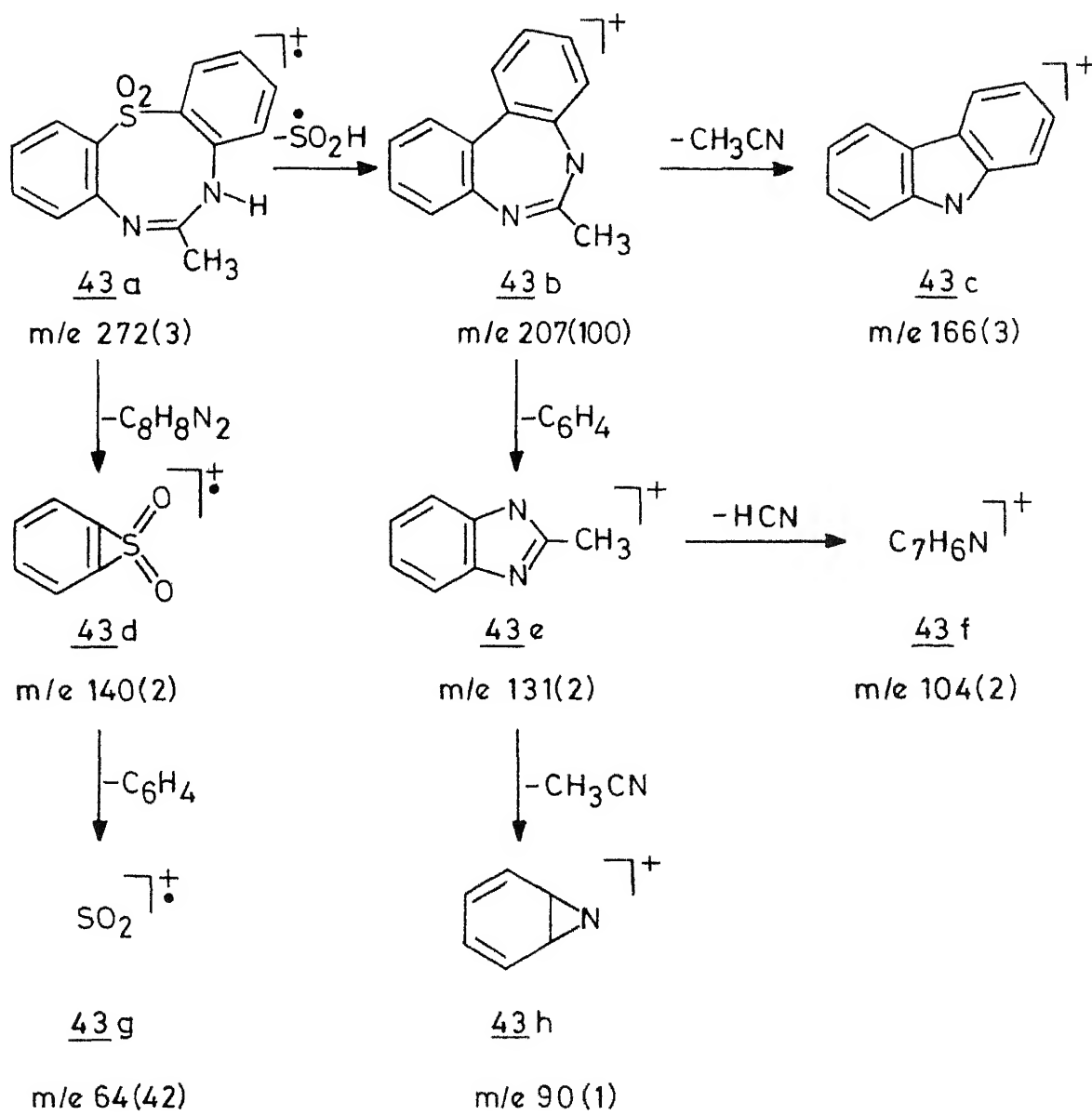


Fig. III. 4 ¹H NMR spectrum (90 MHz) of 43.

Fig III 5 Mass spectrum of 43

Scheme III 9



Further proof for the structure of 43 was derived through its acid-hydrolysis, which resulted in a 74% yield of 2,2'-diaminodiphenyl sulfone (46) (Scheme III.13).

Similarly, the irradiation of 2H-1,2,4-benzothiadiazine-3-methyl-2-(2'-methylphenyl) 1,1-dioxide (34) in methanol gave a 33% yield of 5H-dibenzo[b,g][1,4,6]thiadiazocine-4,6-dimethyl 12,12-dioxide (44), whereas the irradiation in benzene gave a 37% yield of 44. The structure of 44 has been established on the basis of analytical results and spectral data. The ^1H NMR spectrum of 44 (Fig. III.6), for example, showed two sharp singlets at δ 2.19 (3 H) and 2.40 (3 H), due to the two methyl groups at C-4 and C-6 positions. In addition, the spectrum showed a doublet of doublets centred around δ 7.53 (1 H) and 7.77 (1 H), assigned to the H-1 and H-11 protons, respectively. The coupling constants that we have observed for these signals, $J_{1,2} = 8$ Hz, $J_{1,3} = 2$ Hz and $J_{10,11} = 7$ Hz, $J_{9,11} = 2$ Hz, are consistent with the observed couplings for ortho and meta protons in aromatic rings.¹⁴ The remaining aromatic protons appeared as a complex multiplet centred around δ 7.05 (5 H). In addition, there appeared a one proton singlet at δ 9.05 (D_2O -exchangeable) assigned to the NH proton.

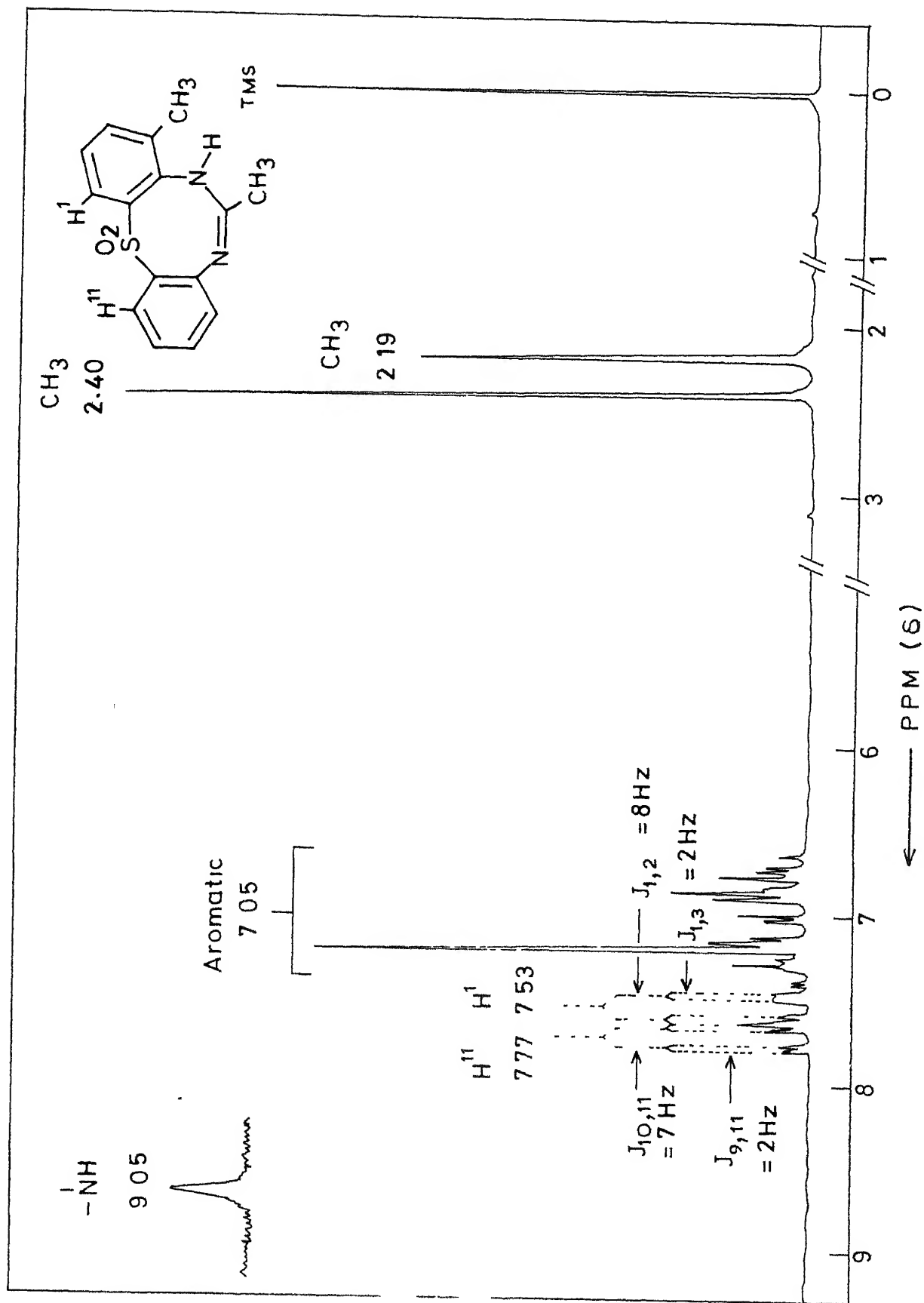
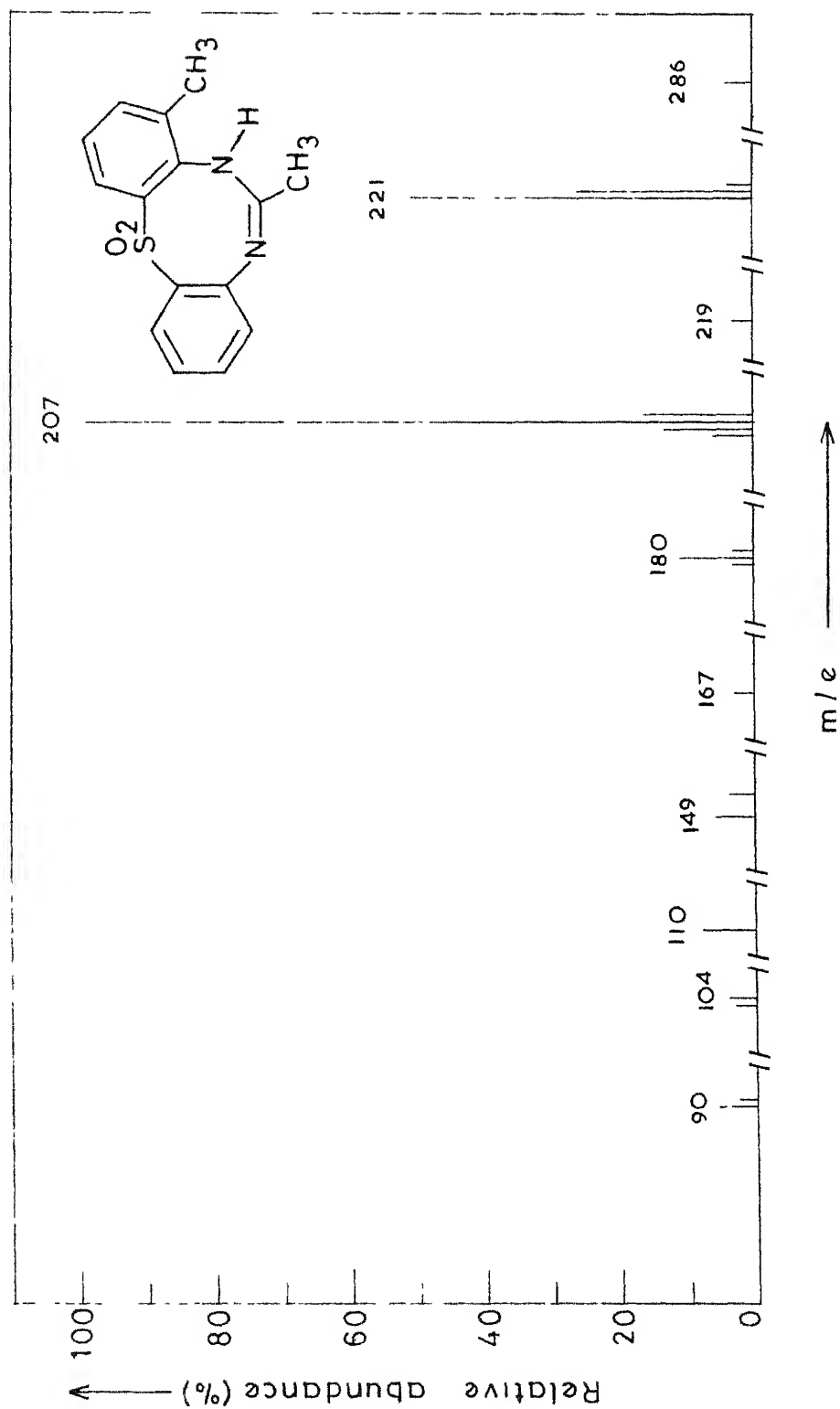


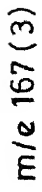
Fig. III 6 1H NMR spectrum (90 MHz) of 44.

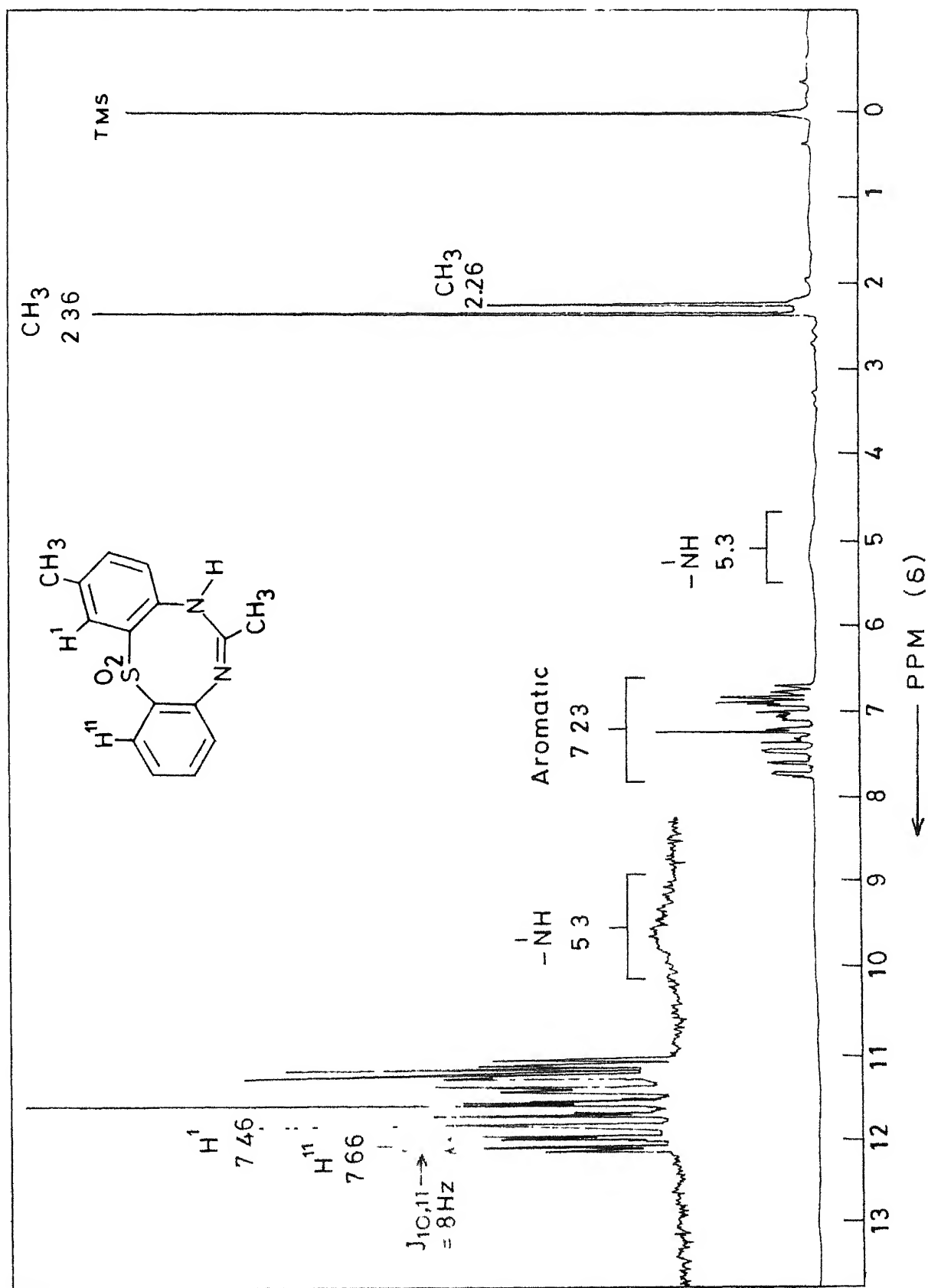
Further evidence concerning the structure of 44 was derived from its mass spectrum. The mass spectrum of 44 (Fig. III.7) showed a molecular ion peak at m/e 286 (6). In addition, the spectrum showed several peaks at m/e 223 (4), 222 (26), 221 (56), 219 (3), 208 (16), 207 (100), 206 (13), 205 (6), 181 (3), 180 (11), 179 (3), 167 (3), 152 (4), 149 (6), 110 (8), 104 (4), 103 (3), 91 (3) and 90 (6). Some of the probable fragmentation modes are shown in Scheme III.10.

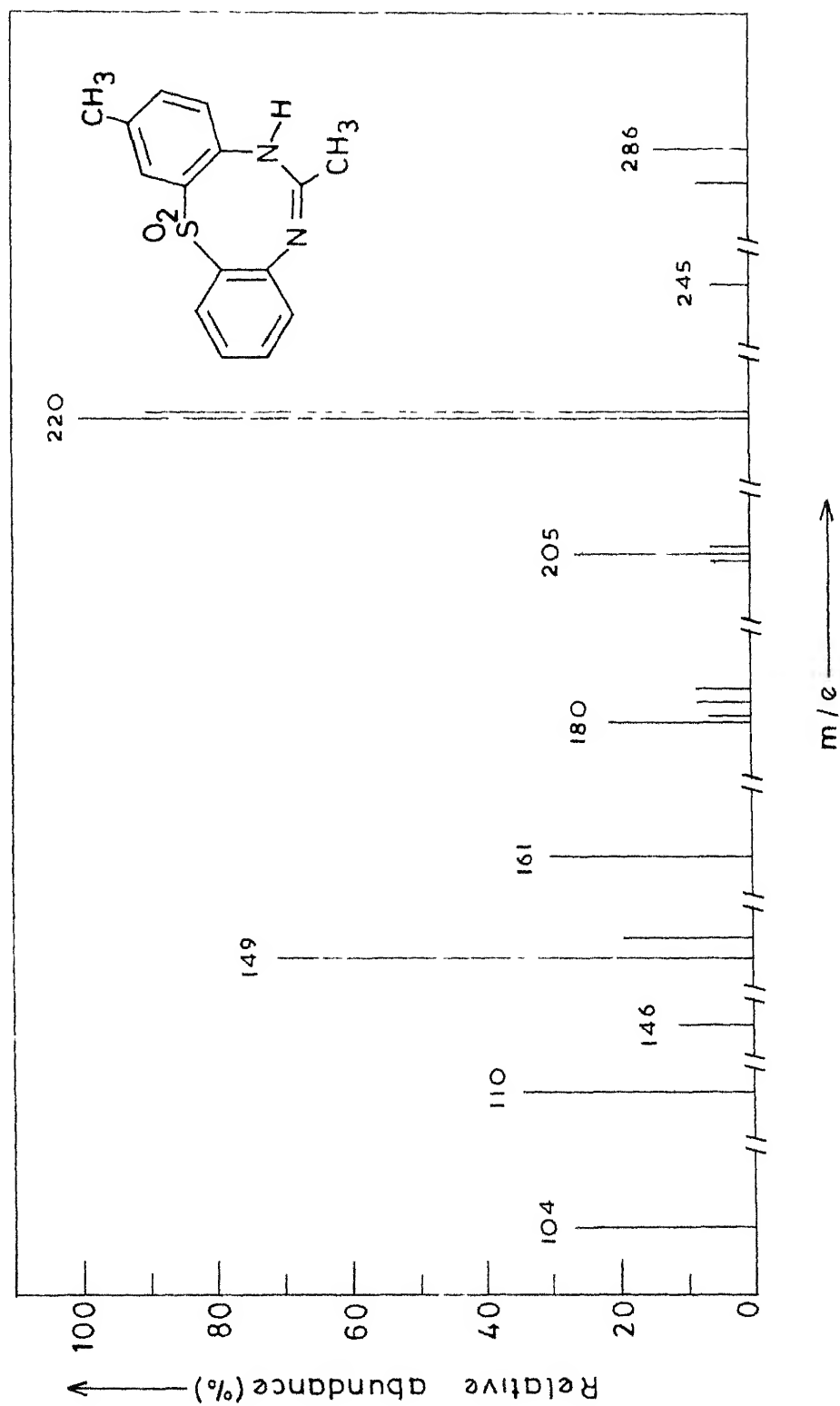
Irradiation of 2H-1,2,4-benzothiadiazine-3-methyl-2-(4'-methylphenyl) 1,1-dioxide (35) in methanol gave a 33% yield of 5H-dibenzo[b,g][1,4,6]thiadiazocine-2,6-dimethyl 12,12-dioxide (45), whereas the irradiation in benzene gave a 46% yield of 45. The structure of 45 has been arrived at on the basis of analytical data and spectral evidences. The ^1H NMR spectrum of 45 (Fig. III.8), for example, showed two singlets at δ 2.26 (3 H) and 2.36 (3 H), due to the two methyl groups and a broad singlet at δ 5.3 (1 H, D_2O -exchangeable) due to the NH proton. In addition, the spectrum showed a complex multiplet centred around δ 7.23 (7 H), which included a doublet of doublets at δ 7.66 (1 H, $J_{10,11} = 8$ Hz and $J_{9,11} = 2$ Hz) and a singlet at δ 7.46 (1 H), assigned to the H-11 and H-1 protons, respectively.

The mass spectrum of 45 (Fig. III.9) showed the molecular ion peak at m/e 286 (14). Other peaks in the spectrum were observed at m/e 281 (8), 245 (6), 221 (85), 220 (100),

Fig III 7 Mass spectrum of 44

Scheme III 10

Fig III. 8 1H NMR spectrum (90 MHz) of 45

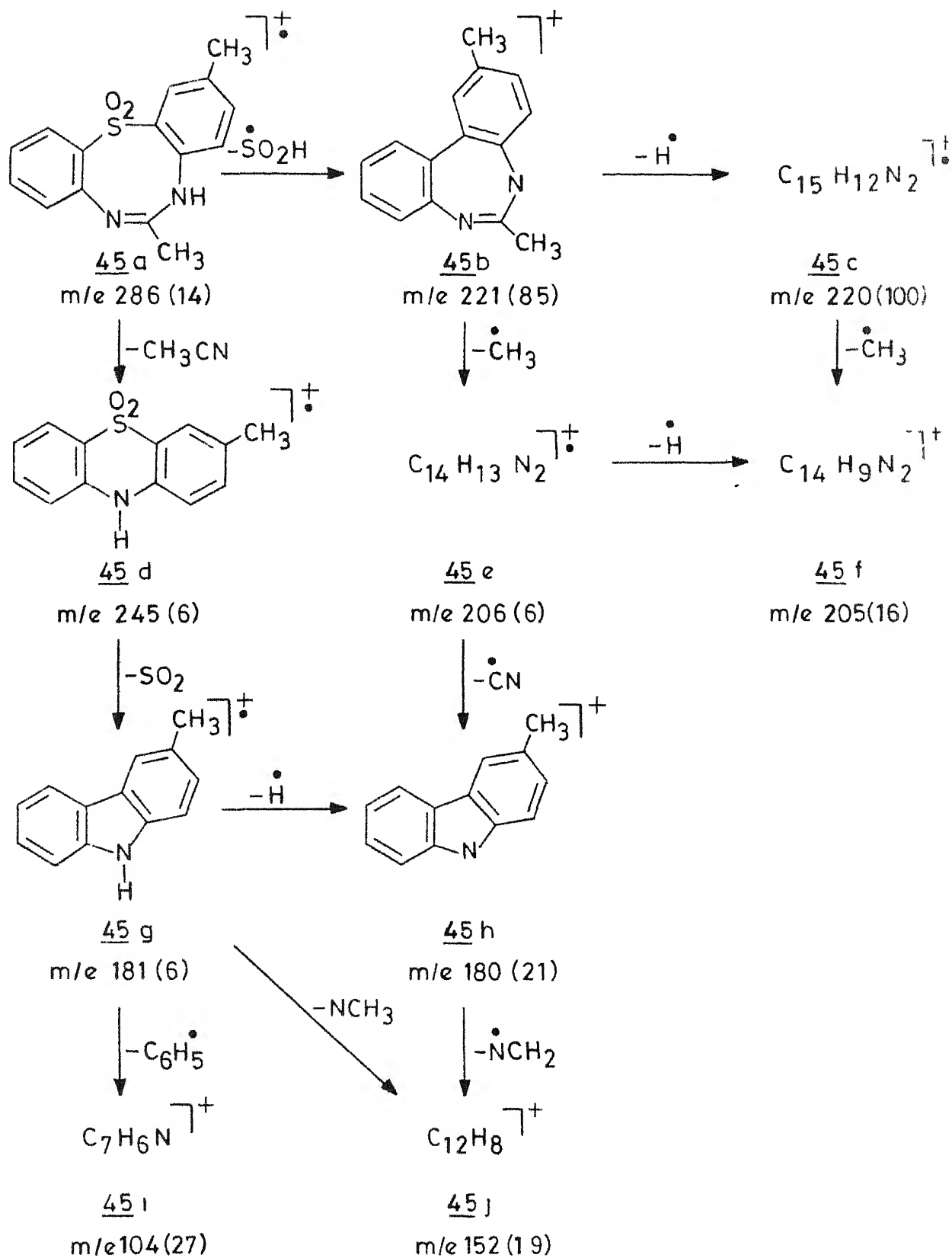
Fig III. 9 Mass spectrum of 45

206 (6), 205 (26), 204 (6), 185 (8), 183 (8), 181 (6), 180 (21), 161 (30), 152 (19), 149 (71), 146 (11), 110 (34) and 104 (27). Some of the prominent fragmentation modes are shown in Scheme III.11.

Additional proof for the structure of 45 was derived through its acid-hydrolysis, which resulted in the isolation of a 64% yield of a product, identified as 2,2'-diamino-5-methyldiphenyl sulfone (47). The ^1H NMR spectrum of 47 (Fig. III.10), for example, showed a singlet at δ 2.21 (3 H), due to the methyl protons and two other singlets at δ 5.53 (2 H) and 5.73 (2 H), which were exchangeable with D_2O and could be assigned to the two amino groups. The spectrum contained a one proton singlet at δ 7.58, assigned to H-6, whereas the H-6' proton appeared as a doublet ($J_{5',6'} = 8$ Hz) centred around δ 7.78. The remaining aromatic protons appeared as a complex multiplet centred around δ 6.98 (5 H).

The formation of different dibenzothiadiazocine dioxides such as 43, 44 and 45 in the photoreactions of the benzothiadiazine dioxides 33, 34 and 35, respectively, can be rationalized in terms of the pathway shown in Scheme III.12. It has been assumed that the thiadiazine dioxides 33-35, on irradiation, undergo homolytic cleavage to give the corresponding biradical intermediates 40a-c, which can subsequently undergo cyclization to give 42a-c. Alternatively, the

Scheme III.11



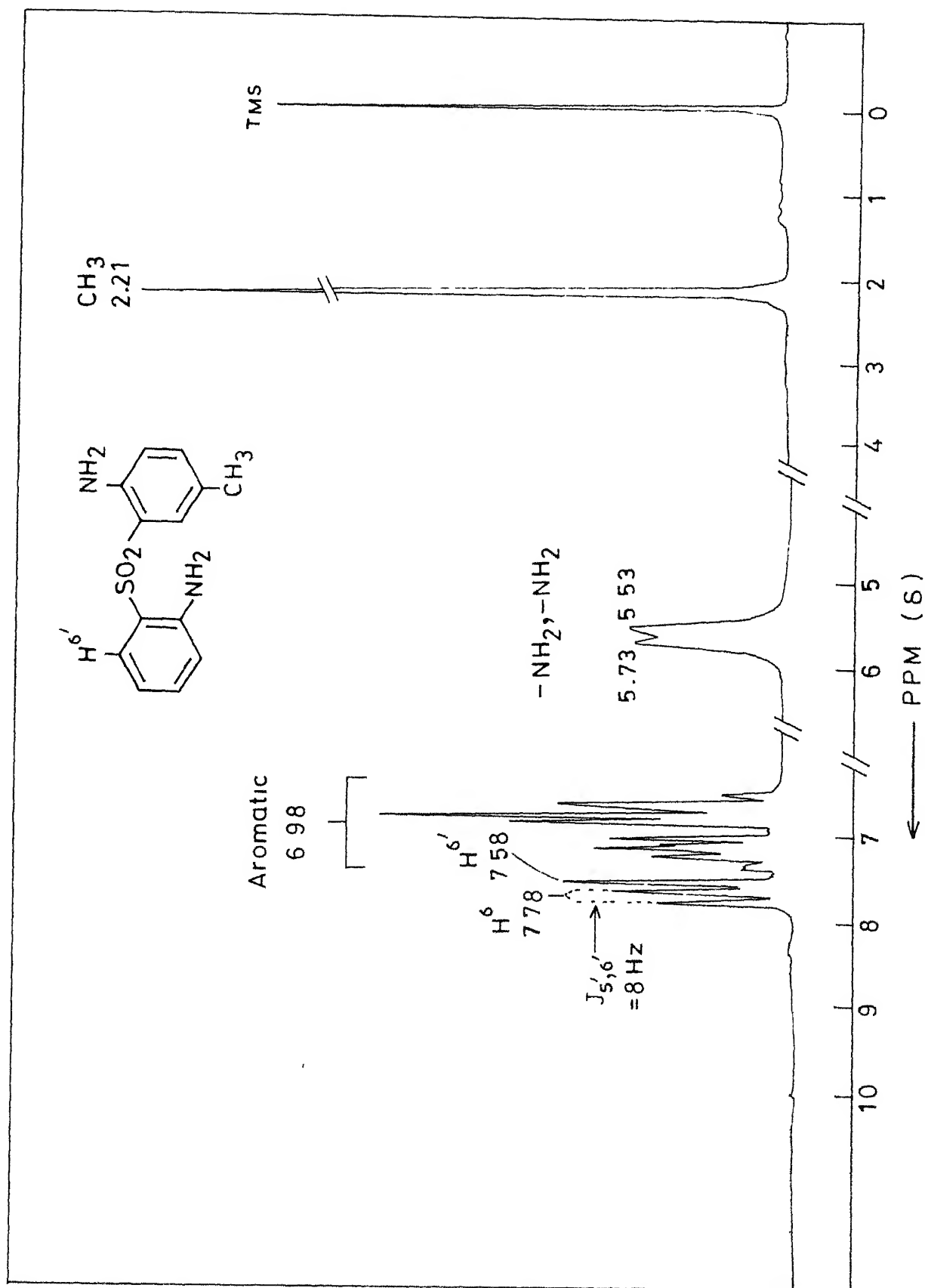
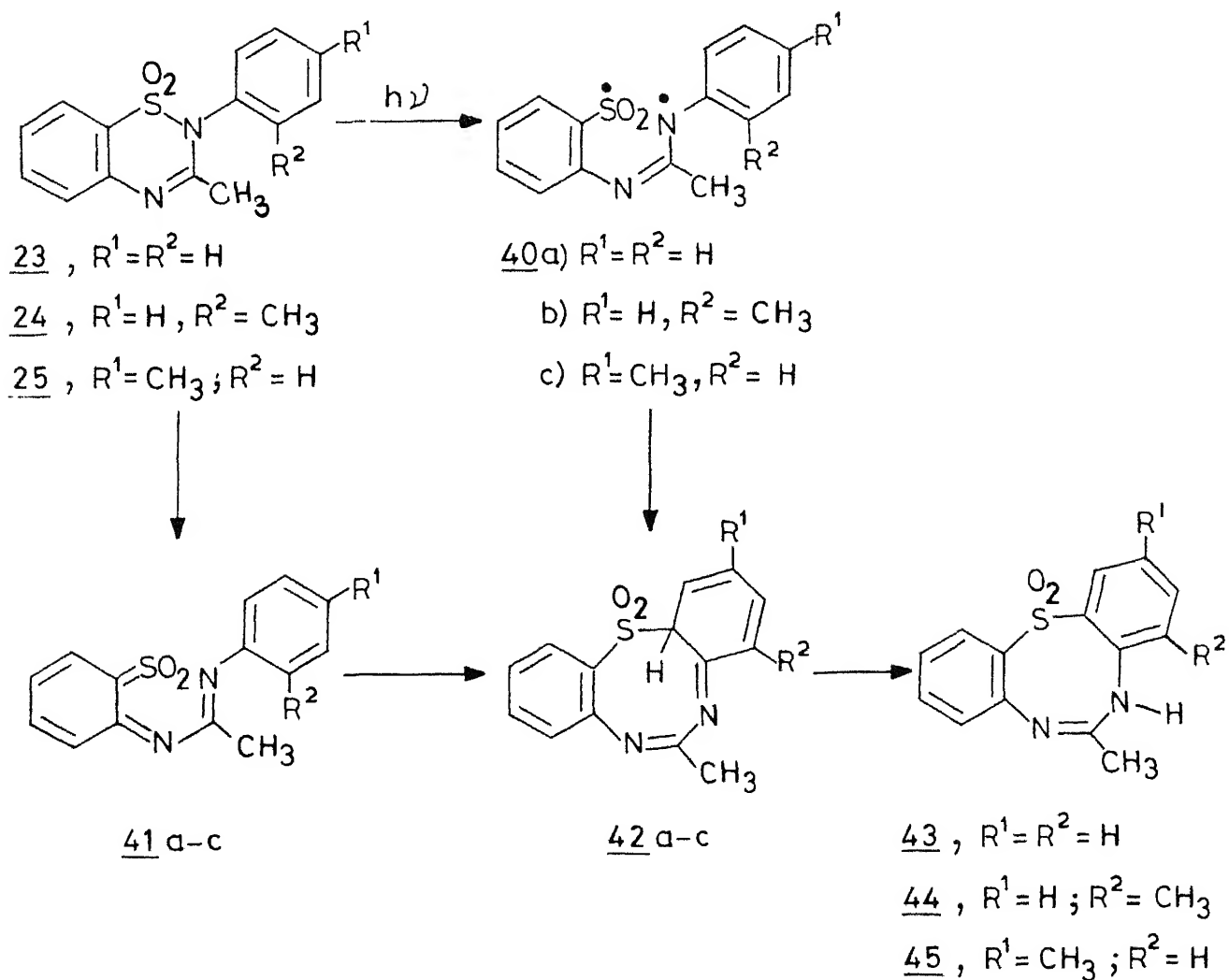
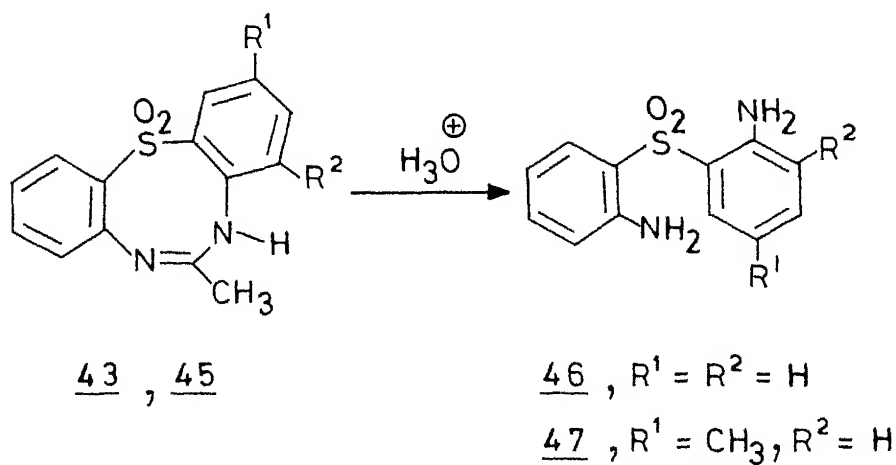


Fig III.10 ^1H NMR spectrum (90 MHz) of 47

Scheme III 12



Scheme III 13



thiadiazine dioxides can undergo ring-opening through a concerted pathway to give the heterohexatrienes 41a-c, which can subsequently undergo photocyclization to give 42a-c. The transformation of 42a-c to the dibenzothiadiazocine dioxides 43-45, can occur through a [1,3] proton shift, either under thermal or photochemical conditions.

III.3.3 Attempted Thermal and Photochemical Transformations of 2H-1,2,4-Benzothiadiazine 1,1-Dioxides

Encouraged by the results of our studies on the photo-transformations of benzothiadiazine 1,1-dioxides leading to ring-expanded products, we have examined the thermal transformations of a few benzothiadiazine 1,1-dioxides such as 2H-1,2,4-benzothiadiazine-2-phenyl 1,1-dioxide (32), 2H-1,2,4-benzothiadiazine-3-methyl-2-phenyl 1,1-dioxide (33), 2H-1,2,4-benzothiadiazine-3-methyl-2-(2'-methylphenyl) 1,1-dioxide (34), 2H-1,2,4-benzothiadiazine-3-methyl-2-(4'-methylphenyl) 1,1-dioxide (35) and 2H-1,2,4-benzothiadiazine-2-cyclohexyl-3-methyl 1,1-dioxide (36).

Thus, heating of 2H-1,2,4-benzothiadiazine-2-phenyl 1,1-dioxide (32) in refluxing diphenyl ether, for 10 hr, for example, resulted in the isolation of a 87% yield of N-(2'-formamidobenzenesulfonyl)aniline (39), as the only isolable product. In contrast, the thermolysis of the thiadiazine 1,1-dioxides 33, 34 and 35, under analogous conditions did not

give rise to any isolable products; the starting materials were recovered, in each case.

The formation of 39 in the thermolysis of 32 may arise through the initial addition of elements of water, under the reaction conditions to give the carbinol intermediate, 38, which can subsequently undergo cleavage to give 39, as shown in Scheme III.8.

Interestingly, the thermolysis of 2H-1,2,4-benzothiadiazine-2-cyclohexyl-3-methyl 1,1-dioxide (36) in refluxing diphenyl ether gave an 82% yield of a product, identified as 2-amino-2,3-dihydro-2-methyl-1,3-benzothiazole 1,1-dioxide (55). The ^1H NMR spectrum of 55 (Fig. III.11), for example, showed a sharp singlet at δ 2.30 (3 H), assigned to the methyl protons and a second singlet at δ 3.38 (2 H, D_2O -exchangeable), assigned to the NH_2 group protons. In addition, the ^1H NMR spectrum showed a complex multiplet centred around δ 7.54 (4 H), due to the aromatic protons.

The mass spectrum of 55 (Fig. III.12), showed a molecular ion peak at m/e 198 (4). In addition, the spectrum showed several signals at m/e 197 (11), 196 (49), 157 (8), 156 (13), 155 (100), 138 (10), 132 (7), 131 (9), 122 (3), 106 (6) and 96 (7). Some of the probable fragmentation pathways are shown in Scheme III.14.

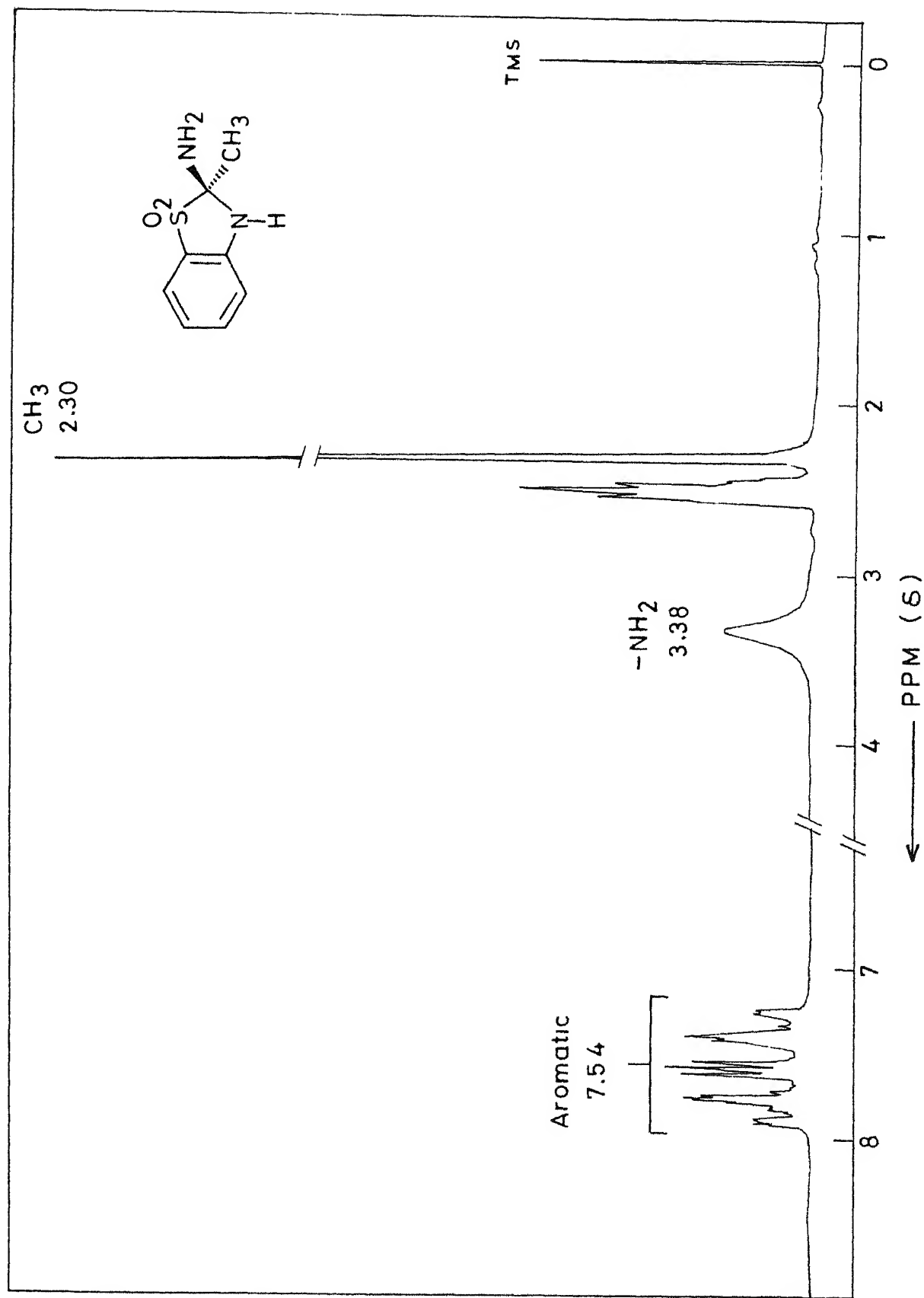


Fig. III 11 ^1H NMR spectrum (90 MHz) of 55

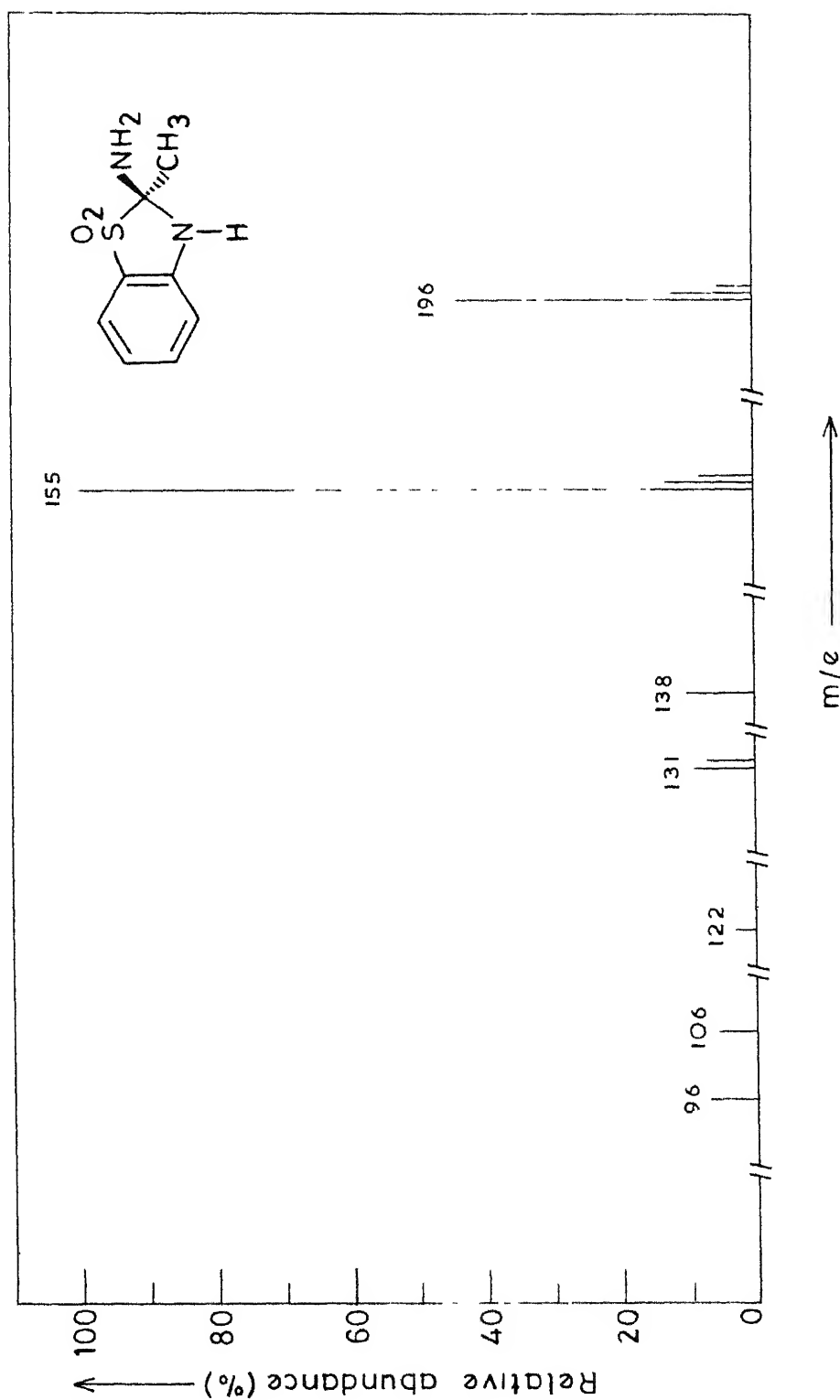


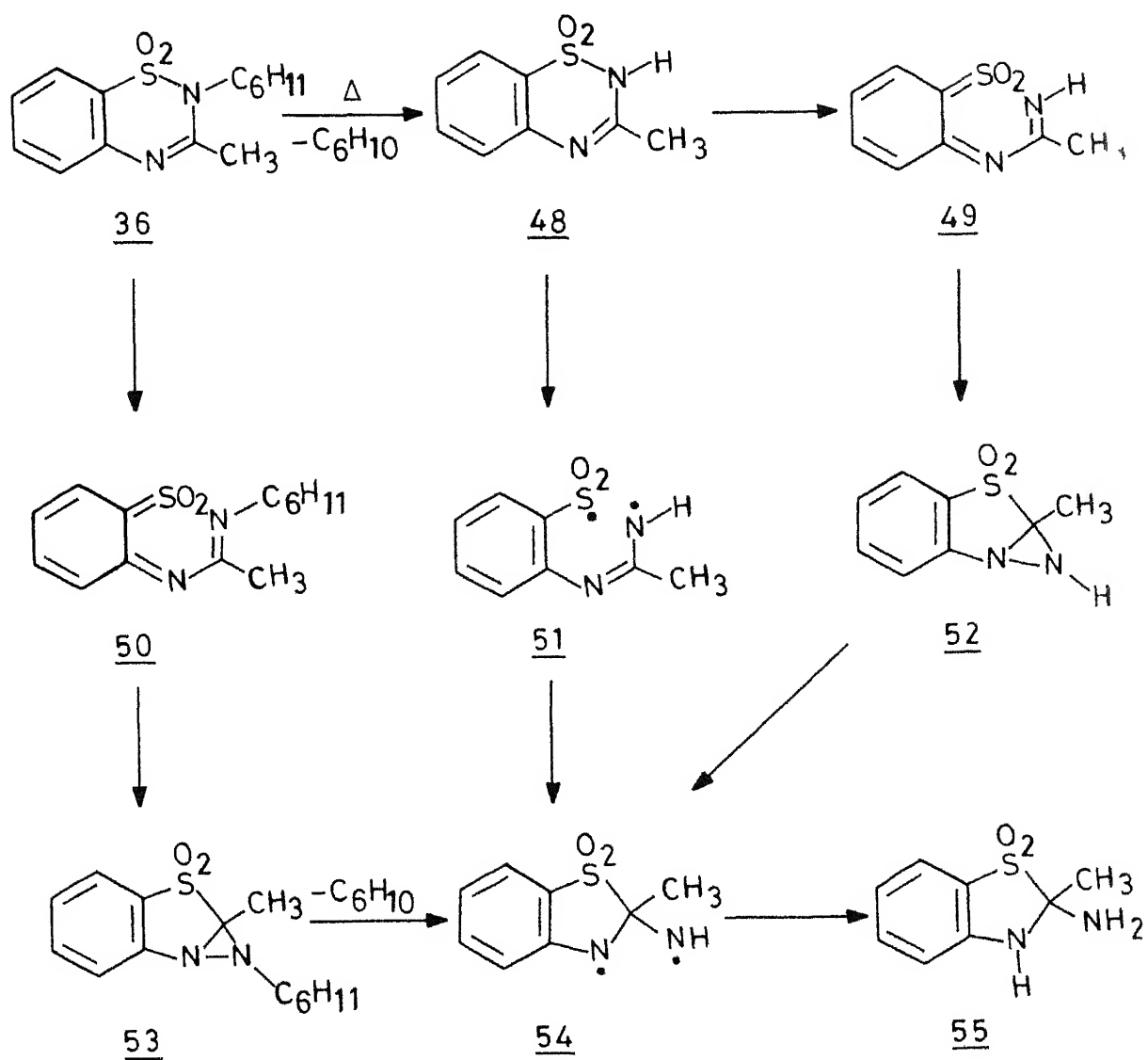
Fig III 12 Mass spectrum of 55

The loss of a hydrogen atom from the molecular ion 55a could give rise to 55b at m/e 197, which in turn can lead to the fragment 55c at m/e 156. On the other hand, the loss of SO_2 and two hydrogen atoms from 55a would result in the fragment 55e at m/e 132, which in turn can lose one more hydrogen atom to give the fragment 55f at m/e 131. If on the other hand, the fragment H_3CCNH_2 is lost from 55a, it would result in the formation of 55d at m/e 155.

The fragmentation patterns indicated in Scheme III.14 are in support of the assumed structure 55, for the thermolysis product derived from 36.

The formation of 55 from 36 may be rationalized in terms of the pathway shown in Scheme III.15. One of the possible pathways involves the initial formation of 48, under thermal conditions, which will then undergo ring-opening to give the heterohexatriene intermediate 49. Further transformation of 49 through the intermediates 52 and 54 will ultimately lead to 55. An alternative pathway for the transformation of 36, involves its conversion to the heterotriene intermediate 50, which subsequently can be transformed to 55, through the intermediates 53 and 54, as shown in Scheme III.15.

Scheme III 15



III.4 EXPERIMENTAL

All melting points are uncorrected and were determined on a Mel-Temp, melting-point apparatus. The IR spectra were recorded on Perkin-Elmer Model 377 or Model 580 infrared spectrophotometer. The electronic spectra were recorded on either Beckman DB or Cary 17D spectrophotometer. NMR traces were recorded on Varian A-60 or Bruker WH-90 NMR spectrometer, using tetramethylsilane as internal standard. The mass spectra were recorded on a Hitachi RMU-6E Single Focussing Mass spectrometer or a Varian Mat CH7 mass spectrometer at 70 eV. All irradiation experiments were carried out in a Srinivasan-Griffin Rayonet photochemical reactor (2537 Å), or by using a Hanovia 450-W medium-pressure mercury lamp in a quartz-jacketed immersion well, with a pyrex filter.

III.4.1 Starting Materials

Triethyl orthoacetate,¹⁶ bp 144-146° and trimethyl orthoacetate,¹⁷ bp 107-109° were prepared by known procedures whereas, triethyl orthoformate obtained from Aldrich was redistilled before use (bp 146°). N-(2'-aminobenzenesulfonyl)-aniline⁷ (25) mp 121-122°, N-(2'-aminobenzenesulfonyl)-2-methylaniline⁷ (26) mp 115-116°, N-(2'-aminobenzenesulfonyl)-4-methylaniline⁷ (27) mp 125-126° and 2-nitrobenzenesulfonyl chloride¹⁸ mp 64-65°, were prepared by reported procedures. Petroleum ether used was the fraction bp 60-80°.

III.4.2 Preparation of 2H-1,2,4-Benzothiadiazine-2-phenyl 1,1-Dioxide (32)

A mixture of N-(2'-aminobenzenesulfonyl)aniline (25) (2.48 g, 10 mmol) and triethyl orthoformate (29) (2.22 g, 15 mmol) was heated around 130-140° for ½ hr and the alcohol that was liberated during the reaction was distilled off. After removal of any unchanged orthoester under reduced pressure, diphenyl ether (25 ml) was added to the reaction mixture and heated under reflux for an additional period of ½ hr. Removal of the solvent under vacuum gave a solid residue, which was washed with petroleum ether and recrystallized from chloroform to give 1.94 g (75%) of 2H-1,2,4-benzothiadiazine-2-phenyl 1,1-dioxide (32), mp 133-134° (lit.⁷ mp 133-134°).

III.4.3 Preparation of 2H-1,2,4-Benzothiadiazine-3-methyl-2-phenyl 1,1-Dioxide (33)

A mixture of N-(2'-aminobenzenesulfonyl)aniline (1.24 g, 5 mmol) and triethyl orthoacetate (30) (1.22 g, 7.5 mmol) was heated around 130-140° for ½ hr and subsequently in diphenyl ether for an additional period of ½ hr. Work-up of the reaction mixture as in the previous case by removal of the solvent under vacuum, washing of the residual solid with petroleum ether and recrystallization from chloroform gave 1.01 g (74%) of 2H-1,2,4-benzothiadiazine-3-methyl-2-phenyl 1,1-dioxide (33), mp 162-163°.

Anal. Calcd for $C_{14}H_{12}N_2O_2S$: C, 61.76; H, 4.41; N, 10.29; Mol. wt., 272. Found: C, 61.90; H, 4.44; N, 9.96; Mol. wt., 272 (Mass spectrometry).

IR spectrum (KBr) ν_{\max} : 3040, 2980 and 2940 cm^{-1} ($\nu_{\text{C-H}}$), 1601 cm^{-1} ($\nu_{\text{C=N}}$), 1575 cm^{-1} ($\nu_{\text{C=C}}$), 1332 and 1060 cm^{-1} (ν_{SO_2}).

UV spectrum (methanol) λ_{\max} : 260 nm (ϵ , 14,100), 270 (11,900, sh) and 297 (8,700, sh).

NMR spectrum (CDCl_3): δ 2.14 (3 H, s, methyl) 7.40 (8 H, m, aromatic) and 7.82 (1 H, d, $J_{7,8} = 7$ Hz, H-8).

III.4.4 Preparation of 2H-1,2,4-Benzothiadiazine-3-methyl-2-(2'-methylphenyl) 1,1-Dioxide (34)

A mixture of N-(2'-aminobenzenesulfonyl)-2-methylaniline (26) (4.7 g, 18 mmol) and triethyl orthoacetate (30) (4.05 g, 25 mmol) was heated around 130-140° for 1/2 hr and later in refluxing diphenyl ether for an additional period of 1/2 hr. Removal of the solvent under vacuum and work-up of the reaction mixture as in the earlier cases gave a product, which was recrystallized from chloroform to give 3.35 g (65%) of 2H-1,2,4-benzothiadiazine-3-methyl-2-(2'-methylphenyl) 1,1-dioxide (34), mp 155-156° (lit.⁷ mp 154-155°).

III.4.5 Preparation of 2H-1,2,4-Benzothiadiazine-3-methyl-2-(4'-methylphenyl) 1,1-Dioxide (35)

Heating of a mixture of N-(2'-aminobenzenesulfonyl)-4-methylaniline (27) (2.62 g, 10 mmol) and trimethyl orthoacetate (31) (1.8 g, 15 mmol), around 130-140° for 1/2 hr and later in refluxing diphenyl ether for an additional period of 1/2 hr, and work-up as in the earlier cases gave 2.1 g, (73%) of 2H-1,2,4-benzothiadiazine-3-methyl-2-(4'-methylphenyl) 1,1-dioxide (35), mp 172-173°, after recrystallization from chloroform.

Anal. Calcd for $C_{15}H_{14}N_2O_2S$: C, 62.94; H, 4.90; N, 9.79. Found: C, 62.89; H, 4.62; N, 9.41.

IR spectrum (KBr) ν_{\max} : 3060, 3020, 2920 and 2860 cm^{-1} ($\nu_{\text{C-H}}$), 1610 cm^{-1} ($\nu_{\text{C=N}}$), 1585 cm^{-1} ($\nu_{\text{C=C}}$), 1330 and 1160 cm^{-1} (ν_{SO_2}).

UV spectrum (methanol) λ_{\max} : 260 nm (ϵ , 15,000), 275 (11,000, sh) and 300 (8,500).

NMR spectrum (CDCl_3): δ 2.1 (3 H, s, methyl), 2.4 (3 H, s, methyl) and 7.6 (9 H, m, aromatic).

III.4.6 Preparation of 2H-1,2,4-Benzothiadiazine-2-cyclohexyl-3-methyl 1,1-Dioxide (36)

To a stirred mixture of pyridine (4.0 g, 64 mmol) and cyclohexylamine (5.5 g, 56 mmol), 2-nitrobenzenesulfonyl chloride (11.0 g, 50 mmol) was added in small portions, over

a period of $\frac{1}{2}$ hr. The reaction mixture was subsequently warmed to around $60-70^{\circ}$ for $\frac{3}{4}$ hr and was then treated with dilute hydrochloric acid (2 N, 150 ml) and the residue obtained was recrystallized from chloroform to give 11.0 g (77%) of N-(2'-nitrobenzenesulfonyl)cyclohexylamine, mp $85-86^{\circ}$.

Anal. Calcd for $C_{12}H_{16}N_2O_4S$: C, 50.76; H, 5.41; N, 9.41. Found: C, 50.70; H, 5.63; N, 9.86.

IR spectrum (KBr) ν_{\max} : 3300 cm^{-1} (ν_{N-H}), 3100, 2930 and 2860 cm^{-1} (ν_{C-H}), 1330 and 1160 cm^{-1} (ν_{SO_2}).

NMR spectrum ($CDCl_3$): δ 1.4 (10 H, m, methylene), 3.2 (1 H, m, methine), 5.1 (1 H, broad, NH) and 7.7 (4 H, m, aromatic).

To a hot solution of N-(2'-nitrobenzenesulfonyl)-cyclohexylamine (11.3 g, 40 mmol) in glacial acetic acid (100 ml), maintained around 70° , was added iron powder (10 g) in small portions over a period of 3 hr. The contents were cooled, filtered and poured over crushed ice. The solid that separated out was washed with water and recrystallized from methanol to give 8.0 g (79%) of N-(2'-aminobenzenesulfonyl)-cyclohexylamine, mp $106-107^{\circ}$.

IR spectrum (KBr) ν_{\max} : 3440 and 3360 cm^{-1} (ν_{N-H} , asymmetric and symmetric), 3290 cm^{-1} (ν_{N-H}), 3060, 2920 and 2840 cm^{-1} (ν_{C-H}), 1320 and 1140 cm^{-1} (ν_{SO_2}).

A mixture of N-(2'-aminobenzenesulfonyl)cyclohexylamine (2.54 g, 10 mmol) and trimethyl orthoacetate (31) (1.80 g, 15 mmol) was heated around 130-140° for 1/2 hr. The reaction mixture, on cooling gave a solid material, which was washed with hexane and recrystallized from carbon tetrachloride to give 2.3 g (74%) of N-(2'-benzenesulfonylcyclohexylamine)acetimino ethyl ether (37e) mp 95-96°.

IR spectrum (KBr) ν_{\max} : 3320 cm^{-1} ($\nu_{\text{N-H}}$), 3060, 3010, 2920 and 2840 cm^{-1} ($\nu_{\text{C-H}}$), 1660 cm^{-1} ($\nu_{\text{C=N}}$), 1280 and 1160 cm^{-1} (ν_{SO_2}).

A solution of N-(2'-benzenesulfonylcyclohexylamine)-acetimino ethyl ether (37e) (2.5 g, 0.8 mmol) in 1,2-dichlorobenzene (25 ml) was heated to reflux for 2 hr and later the solvent was removed under vacuum to give a residual solid, which was washed with petroleum ether and recrystallized from carbon tetrachloride to give 1.54 g (69%) of 2H-1,2,4-benzothiadiazine-2-cyclohexyl-3-methyl 1,1-dioxide (36), mp 122-123°.

Anal. Calcd for $\text{C}_{14}\text{H}_{18}\text{N}_2\text{O}_2\text{S}$: C, 60.43; H, 6.47; N, 10.07; Mol. wt., 278. Found: C, 59.98; H, 5.94; N, 10.38; Mol. wt., 278 (Mass spectrometry).

IR spectrum (KBr) ν_{\max} : 3020, 2990, 2920 and 2860 cm^{-1} ($\nu_{\text{C-H}}$), 1570 cm^{-1} ($\nu_{\text{C=N}}$), 1320 and 1180 cm^{-1} (ν_{SO_2}).

UV spectrum (methanol) λ_{\max} : 260 nm (ϵ , 2,300) and 297 (2,200).

NMR spectrum (CDCl_3): δ 1.55 (10 H, m, methylene), 2.56 (3 H, s, methyl), 3.97 (1 H, m, H-1') and 7.55 (4 H, m, aromatic).

Mass spectrum m/e (relative intensity): 278 (21), 236 (4), 212 (7), 199 (6), 198 (21), 197 (52), 196 (100), 163 (3), 156 (54), 155 (55), 149 (5), 138 (9), 137 (8), 133 (15), 132 (40), 131 (27), 130 (12), 118 (10), 117 (39), 116 (10), 108 (10), 107 (9), 106 (10) and 98 (18).

III.4.7 Irradiation of 2H-1,2,4-Benzothiadiazine-2-phenyl 1,1-Dioxide (32) in Methanol

A solution of 32 (222 mg, 0.86 mmol) in methanol (220 ml) was irradiated for 1 hr using a 450-W Hanovia medium-pressure mercury lamp, provided with a pyrex filter. The photolysis was repeated thrice, to irradiate, in all, 888 mg (3.4 mmol) of 32. Removal of the solvent from the combined photolysates under vacuum gave a product mixture, which was chromatographed over silica gel. Elution with a mixture (1:1) of petroleum ether and benzene gave 605 mg (72%) of N-(2'-aminobenzenesulfonyl)aniline (25), mp 121-122° (mixture melting point), after recrystallization from chloroform.

Further elution of the column with a mixture (4:1) of petroleum ether and ethyl acetate, gave 75 mg (8%) of N-(2'-formamidobenzenesulfonyl)aniline (39), mp 151-152° after recrystallization from chloroform.

Anal. Calcd for $C_{13}H_{12}N_2O_3S$: C, 56.52; H, 4.35; N, 10.14; Mol. wt., 276. Found: C, 56.39; H, 4.30; N, 10.38; Mol. wt., 276 (Mass spectrometry)

IR spectrum (KBr) ν_{\max} : 3325 cm^{-1} (ν_{N-H}), 3160 and 3080 cm^{-1} (ν_{N-H}), 2900 cm^{-1} (ν_{C-H}), 1680 cm^{-1} ($\nu_{C=O}$), 1340 and 1150 cm^{-1} (ν_{SO_2}).

UV spectrum (ethanol) λ_{\max} : 280 nm (ϵ , 5,250) and 246 (21,900).

III.4.8 Irradiation of 2H-1,2,4-Benzothiadiazine-2-phenyl 1,1-Dioxide (32) in Benzene

A solution of 32 (222 mg, 0.86 mmol) in benzene was irradiated in a Srinivasan-Griffin Rayonet photochemical reactor using a 2537 \AA light source for 1.6 hr. The irradiation was repeated once again, to photolyse in all, 444 mg (1.72 mmol) of 32. Removal of the solvent under vacuum from the combined photolysates gave a product mixture, which was chromatographed over silica gel. Elution with a mixture (4:1) of petroleum ether and benzene gave 43 mg (10%) of the unchanged starting material (32), mp $133-134^\circ$ (mixture melting point). Further elution of the column with a mixture (4:1) of petroleum ether and ethyl acetate, gave 323 mg (68%) of N-(2'-formamido-benzenesulfonyl)aniline (39), mp $151-152^\circ$ after recrystallization from chloroform.

III.4.9 Reaction of N-(2'-Aminobenzenesulfonyl)aniline (25) with Formic Acid

A mixture of 25 (250 mg, 1 mmol) and formic acid (85%, 2 ml) was heated around 75-80° for 3 hr and was poured over crushed ice. The solid material that separated was filtered, washed with water and later recrystallized from chloroform to give 195 mg, (71%) of N-(2'-formamidobenzene-sulfonyl)aniline, mp 151-152° (mixture melting point).

III.4.10 Irradiation of N-(2'-Formamidobenzenesulfonyl)-aniline (39) in Methanol

A solution of 39 (220 mg, 0.8 mmol) in methanol (220 ml) was irradiated for 1 hr using a 450-W Hanovia medium-pressure mercury lamp, provided with a pyrex filter. Removal of the solvent under vacuum gave a residual solid, which was recrystallized from chloroform to give 140 mg (71%) of N-(2'-aminobenzenesulfonyl)aniline (25), mp 121-122° (mixture melting point).

III.4.11 Irradiation of 2H-1,2,4-Benzothiadiazine-2-phenyl-3-methyl 1,1-Dioxide (33) in Methanol

A solution of 33 (185 mg, 0.68 mmol) in methanol (180 ml) was irradiated for 2 hr, in a Srinivasan-Griffin Rayonet photochemical reactor using a 2537 Å light source. The photolysis was repeated twice and the solvent from the combined photolysates was removed under vacuum to give a residual solid, which was chromatographed over alumina. Elution with a mixture (1:9)

of benzene and petroleum ether gave 225 mg (40%) of the unchanged starting material (33), mp 162-163° (mixture melting point), after recrystallization from chloroform.

Further elution of the column with a mixture (1:3) of petroleum ether and benzene gave 242 mg (44%) of 5H-dibenzo-[b,g][1,4,6]thiadiazocine-6-methyl 12,12-dioxide (43), mp 214-215°, after recrystallization from acetone.

Anal. Calcd for $C_{14}H_{12}N_2O_2S$: C, 61.76; H, 4.44; N, 10.29; Mol. wt., 272. Found: C, 61.30; H, 4.79; N, 10.02; Mol. wt., 272 (Mass spectrometry).

IR spectrum (KBr) ν_{\max} : 3320 cm^{-1} ($\nu_{\text{N-H}}$), 3060 cm^{-1} ($\nu_{\text{C-H}}$), 1690 cm^{-1} ($\nu_{\text{C=N}}$), 1330 and 1150 cm^{-1} (ν_{SO_2}).

UV spectrum (ethanol) λ_{\max} : 254 nm (ϵ , 17,000), 300 (6,700) and 350 (250).

III.4.12 Irradiation of 2H-1,2,4-Benzothiadiazine-3-methyl-2-phenyl 1,1-Dioxide (33) in Benzene

A solution of 33 (400 mg, 1.47 mmol) in benzene (300 ml) was irradiated for 2½ hr in a Srinivasan-Griffin Rayonet photochemical reactor, using a 2537 Å lamp source. Removal of the solvent under vacuum from the reaction mixture gave a residual solid, which was chromatographed over neutral alumina. Elution with a mixture (1:9) of benzene and petroleum ether gave 201 mg (50%) of the unchanged starting material (33), mp 162-163° (mixture melting point), after recrystallization

from chloroform. Further elution of the column with a mixture (1:8) of benzene and petroleum ether gave 100 mg (25%) of 43, mp 214-215^o (mixture melting point), after recrystallization from acetone.

III.4.13 Acid-Hydrolysis of 5H-Dibenzo[b,g][1,4,6]-thiadiazocine-6-methyl 12,12-Dioxide (43)

A mixture of 43 (50 mg, 0.18 mmol) and aqueous hydrochloric acid (25%, 1 ml) was heated around 40-50^o for 3 hr. The reaction mixture, on cooling was neutralised with ammonia solution and the precipitate thus resulted was filtered off and recrystallized from acetone to give 33 mg (74%) of 2,2'-diaminodiphenyl sulfone (46), mp 145^o (lit.¹⁹ mp 146^o).

III.4.14 Irradiation of 2H-1,2,4-Benzothiadiazine-3-methyl-2-(2'-methylphenyl) 1,1-Dioxide (34) in Methanol

A solution of 34 (200 mg, 0.7 mmol) in methanol (180 ml) was irradiated for 4 hr in a Srinivasan-Griffin Rayonet photochemical reactor using a 2537 Å lamp source. The irradiation was repeated twice, to photolyse, in all, 600 mg (2.1 mmol) of 34. Removal of the solvent under vacuum from the combined photolysates gave a residual solid, which was chromatographed over neutral alumina. Elution with a mixture (1:9) of benzene and petroleum ether gave 250 mg (42%) of the unchanged starting material (34), mp 154-155^o (mixture melting point), after recrystallization from chloroform.

Subsequent elution of the column with a mixture (1:3) of benzene and petroleum ether gave, 200 mg (33%) of 5H-di-benzo[b,g] [1,4,6] thiadiazocine-4,6-dimethyl 12,12-dioxide (44), mp 238-239°, after recrystallization from acetone.

Anal. Calcd for $C_{15}H_{14}N_2O_2S$: C, 62.94; H, 4.89; N, 9.79; Mol. wt., 286. Found: C, 62.58, H, 4.55; N, 9.68; Mol. wt., 286 (Mass spectrometry).

IR spectrum (KBr) ν_{\max} : 3364 cm^{-1} ($\nu_{\text{N-H}}$), 2916 cm^{-1} ($\nu_{\text{C-H}}$), 1684 cm^{-1} ($\nu_{\text{C=N}}$), 1564 cm^{-1} ($\nu_{\text{C=C}}$), 1355 and 1164 cm^{-1} (ν_{SO_2}).

UV spectrum (ethanol) λ_{\max} : 254 nm (ϵ , 17,200), 301 (6,800) and 350 (200).

III.4.15 Irradiation of 2H-1,2,4-Benzothiadiazine-3-methyl-2-(2'-methylphenyl) 1,1-Dioxide (34) in Benzene

A solution of 34 (192 mg, 0.67 mmol) in benzene (180 ml) was irradiated for 3 hr in a Srinivasan-Griffin Rayonet photochemical reactor, using a 2537 Å light source. The photolysis was repeated twice to irradiate, in all, 576 mg (2.0 mmol) of 34. Removal of the solvent under vacuum gave a residual solid, which was chromatographed over neutral alumina. Elution with a mixture (1:9) of benzene and petroleum ether gave 200 mg (35%) of the unchanged starting material (34), mp 154-155° (mixture melting point), after recrystallization from

chloroform. Subsequent elution of the column with a mixture (1:3) of benzene and petroleum ether gave 212 mg (37%) of 44, mp 238-239° (mixture melting point).

III.4.16 Irradiation of 2H-1,2,4-Benzothiadiazine-3-methyl-2-(4'-methylphenyl) 1,1-Dioxide (35) in Methanol

A solution of 35 (1.0 g, 3.5 mmol) in methanol (350 ml) was irradiated for 16 hr in a Srinivasan-Griffin Rayonet photochemical reactor provided with a 2537 Å lamp source. The solvent was removed under vacuum and the residual solid was chromatographed over alumina. Elution with a mixture (1:9) of benzene and petroleum ether gave 450 mg (45%) of the unchanged starting material (35), mp 172-173° (mixture melting point), after recrystallization from chloroform. Subsequent elution of the column with a mixture (1:3) of benzene and petroleum ether gave 300 mg (30%), of 5H-1,2,4-dibenzo[b,g][1,4,6]thiadiazocine-2,6-dimethyl 12,12-dioxide (45), mp 226°, after recrystallization from acetone.

Anal. Calcd for $C_{15}H_{14}N_2O_2S$: C, 62.94; H, 4.89; N, 9.79; Mol. wt., 286. Found: C, 63.39; H, 4.76; N, 9.77; Mol. wt., 286 (Mass spectrometry).

IR spectrum (KBr) ν_{\max} : 3340 cm^{-1} ($\nu_{\text{N-H}}$), 3070, 3040, 2980 and 2930 cm^{-1} ($\nu_{\text{C-H}}$), 1680 cm^{-1} ($\nu_{\text{C=N}}$), 1310 and 1170 cm^{-1} (ν_{SO_2}).

UV spectrum (methanol) λ_{\max} : 250 nm (ϵ , 39,800), 300 (10,100) and 350 (900).

III.4.17 Irradiation of 2H-1,2,4-Benzothiadiazine-3-methyl-2-(4'-methylphenyl) 1,1-Dioxide (35) in Benzene

A solution of 35 (1.0 g, 3.5 mmol) in benzene (350 ml) was irradiated for 16 hr, as in the previous experiment. Work-up of the reaction mixture by removal of the solvent under vacuum gave a solid residue, which was chromatographed over neutral alumina. Elution of the column with a mixture (1:9) of benzene and petroleum ether gave 400 mg (40%) of the unchanged starting material (35), mp 172-173°, after recrystallization from chloroform.

Further elution of the column with a mixture (1:3) of benzene and petroleum ether gave 460 mg (46%) of 5H-1,2,4-dibenzo[b,g][1,4,6]thiadiazocine-2,6-dimethyl 12,12-dioxide (45), mp 226° (mixture melting point), after recrystallization from acetone.

III.4.18 Acid-Hydrolysis of 5H-1,2,4-Dibenzo[b,g][1,4,6]-thiadiazocine-2,6-dimethyl 12,12-Dioxide (45)

A mixture of 45 (60 mg, 0.21 mmol) and dilute (25%) hydrochloric acid (2 ml) was heated around 40-60° for 3 hr. The reaction mixture was neutralized with ammonia and the precipitated solid was filtered off, washed with water and recrystallized from acetone to give 35 mg (64%) of 2,2'-diamino-5-methyldiphenyl sulfone (47), mp 184°.

Anal. Calcd for $C_{13}H_{14}N_2O_2S$: C, 59.54; H, 5.34; N, 10.69; Mol. wt., 262. Found: C, 59.78; H, 5.40; N, 10.12; Mol. wt., 262 (Mass spectrometry).

IR spectrum (KBr) ν_{\max} : 3480, 3380 and 3220 cm^{-1} ($\nu_{\text{N-H}}$), 3050 and 2920 cm^{-1} ($\nu_{\text{C-H}}$), 1620 cm^{-1} (ν_{NH_2}), 1310 and 1130 cm^{-1} (ν_{SO_2}).

Mass spectrum m/e (relative intensity): 262 (51), 226 (6), 197 (32), 196 (35), 195 (6), 183 (15), 181 (39), 167 (38), 149 (100), 122 (11), 113 (18), 112 (19), 106 (29), 104 (27) and 93 (21).

III.4.19 Thermolysis of 2H-1,2,4-Benzothiadiazine-2-phenyl 1,1-Dioxide (32) in Diphenyl Ether

A solution of 32 (800 mg, 3.10 mmol) in diphenyl ether (10 ml) was heated to reflux for 10 hr. The solvent was removed under vacuum and the residue was washed with petroleum ether to give 744 mg (87%) of N-(2'-formamido-benzenesulfonyl)aniline (39), mp 151-152° (mixture melting point), after recrystallization from chloroform.

III.4.20 Attempted Thermolysis of 2H-1,2,4-Benzothiadiazine-3-methyl-2-phenyl 1,1-Dioxide (33) in Diphenyl Ether

A solution of 33 (300 mg, 1.1 mmol) in diphenyl ether (4 ml) was refluxed for 9 hr. Removal of the solvent under vacuum gave a residual solid, which was recrystallized from chloroform to give 250 mg (83%) of the unchanged starting material (33), mp 161-162° (mixture melting point).

III.5 REFERENCES

1. For the formation of six-membered aromatic and heteroaromatic rings, see, J. C. Jutz, Topics in Current Chemistry, 73, 125 (1978).
2. For a recent review on the thermal and photochemical transformations of heterohexa-1,3,5-trienes, see, M. V. George, A. Mitra and K. B. Sukumaran, Angew. Chem., 92, 1005 (1980); Angew. Chem. Internat. Ed., 19, 973 (1980).
3. For a recent review on the pentadienyl anion cyclizations, see, R. Huisgen, Angew. Chem., 92, 979 (1980); Angew. Chem. Internat. Ed., 19, 947 (1980).
4. E. Gorewit and M. Rosenblum, J. Org. Chem., 38, 2257 (1973).
5. T. Durst and J. F. King, Can. J. Chem., 44, 1869 (1966).
6. T. L. Gilchrist, C. J. Harris, M. E. Peck and C. W. Rees, Chem. Commun., 962 (1975).
7. J. H. Freeman and E. C. Wagner, J. Org. Chem., 16, 815 (1951).
8. L. Raffa, M. Di Bella, L. Di Bella and G. Conti, Farmaco (Pavia), Ed. Sci., 19, 425 (1964); Chem. Abstr., 61, 12475 (1964).
9. G. Kresse, C. Seyfried and A. Trede, Tetrahedron Lett., 3933 (1965).
10. E. Fernand, U. S. Patent, 3,290,302 (1966); Chem. Abstr., 66, 55528 (1967).
11. G. Kresse, C. Seyfried and A. Trede, Justus Liebigs Ann. Chem., 715, 223 (1968); Chem. Abstr., 69, 96681 (1968).

12. M. Ghelardoni, V. Pestellini and F. Russo, Ann. Chim., 59, 590 (1969); Chem. Abstr., 71, 101829 (1969).
13. A. M. Kirkion-Rzeszotarski, J. R. Plimmer, S. V. Krees and W. J. Rzeszotarski, J. Heterocycl. Chem., 12, 155 (1975).
14. R. M. Silverstein, C. G. Bassler and T. C. Morrill, "Spectrometric Identification of Organic Compounds", Third Edition, John Wiley and Sons, Inc., New York, 1974, p.214.
15. G. N. Porter and J. Baldas, "Mass Spectrometry of Heterocyclic Compounds", Wiley Interscience, New York, 1971, p.458.
16. S. M. McElvain and J. W. Nelson, J. Am. Chem. Soc., 64, 1825 (1942).
17. P. P. T. Sah, J. Am. Chem. Soc., 50, 516 (1928).
18. A. I. Vogel, "Practical Organic Chemistry", Third Edition, ELBS and Langman Group Ltd., 1973, p.588.
19. W. J. Evans and S. Smiles, J. Chem. Soc., 181 (1935).

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